EXPERIMENTAL

The electronic absorption spectra were obtained with a Specord UV-vis Spectrophotometer. The synthesis of the 1,2,4-triazoles was described in [6-8].

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THERMOYLYSIS OF 1-PHENYL-5-ALKYLSULFONYLTETRAZOLE IN THE PRESENCE OF ARYLHYDRAZINES. AN INSTANCE OF MIGRATION OF AN ALKYLSULFONYL GROUP IN A 1,3-DIPOLE

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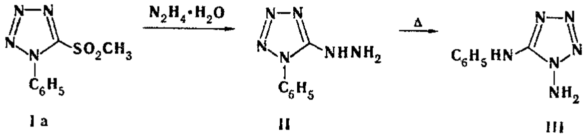
When 1-phenyl-5-alkylsulfonyltetrazoles are heated with arylhydrazines, the heteroring is cleaved to give nitrogen and 1-arylamino-2-phenyl-3-alkylsulfonylguanidine. According to the proposed scheme, the intermediate product of nucleophilic addition of the arylhydrazine to the tetrazole decomposes to give nitrogen and a 1,3-dipole, which is stabilized by migration of an alkylsulfonyl group.

It has previously been shown that the product of replacement of the methylsulfonyl group of 1-phenyl-5-methylsulfonyltetrazole (Ia) by a hydrazino group on heating (100-130°C) is recyclized to the isomeric 1-amino-5-anilinotetrazole (III) [1]:



It seemed of interest to ascertain the scope of this transformation for the reaction of sulfone Ia with other nucleophilic agents, particularly arylhydrazines. It was found that the reaction with phenylhydrazine commences only at 170° and proceeds vigorously at 180-190° with nitrogen evolution. A reaction product with empirical formula $C_{14}H_{16}N_4O_2S$ was isolated in 30% yield from the reaction mixture. The IR spectrum of crystals of the product contain two high-intensity bands at 1253 and 1112 cm^{-1}, which are characteristic for the SO_2 group in sulfones [2]; there are similar bands in the spectrum of starting sulfone Ia (1312 and 1160 cm^{-1}). Absorption bands of stretching and deformation vibrations of NH groups are observed in the IR spec-

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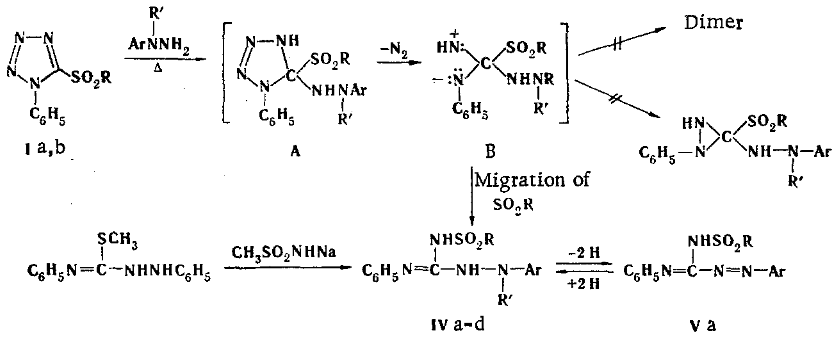
trum of IVa at 3330 (s), 3287 (s), 1603 (vs), and 1562 cm^{-1} (m). The reaction of phenylhydrazine with 1-phenyl-5-ethylsulfonyltetrazole (Ib) and of sulfone Ia with p-chlorophenylhydrazine proceed similarly. This indicates that compounds containing alkylsulfonyl and arylhydrazino groupings are formed in the reaction of sulfones I with arylhydrazines by cleavage of the tetrazole ring.

Starting sulfone Ia is stable at 180-190°, and decomposition occurs only in the presence of an arylhydrazine. In analogy with the reaction of sulfone I with hydrazine hydrate [1] it may be assumed that nucleophilic attack at the carbon atom of the tetrazole ring occurs initially. The intermediate addition product – tetrazoline A – then decomposes at high temperatures to give molecular oxygen and 1,3-dipole B (the formation of 1,3-dipoles during the thermolysis of tetrazoles is known in other cases [3]). The maximum possible delocalization in dipole B is ensured by the unshared pair of electrons of the nitrogen atom bonded to the phenyl ring:



I, IV, Va R=CH$_3$, R′=H, Ar=C$_6$H$_5$; I, IVb R=C$_2$H$_5$, R′=H, Ar=C$_6$H$_5$; IVc R=CH$_3$, R′=H, Ar=p-ClC$_6$H$_4$; d R=CH$_3$, R′=CH$_3$, Ar=C$_6$H$_5$

The 1,3-dipole could be stabilized in the absence of a dipolarophile via three pathways. A hexahydrotetrazine ring could be formed during its dimerization, but this is contradicted by the molecular weight (corresponding to the monomer) found for the product of the reaction of Ia with phenylhydrazine. One might have assumed the formation of a covalent bond between the nitrogen atoms, and this would lead to a diaziridine. However, this sort of structure was rejected on the basis of the ^{13}C NMR data: The ^{13}C NMR spectrum does not contain a signal corresponding to the chemical shift of a three-membered ring, which lies in the region of ordinary sp^3 carbon atoms. This was confirmed by comparison with the ^{13}C spectrum of specially synthesized cyclohexyldiaziridine. In accordance with the third assumption, the 1,3-dipole is stabilized through migration of the electronegative alkylsulfonyl group from the carbon atom to the vicinal positively charged nitrogen atom to give 1-arylamino-2-phenyl-3-alkylsulfonylguanidine (IV). This is the first observation of this sort of migration (a 2,3-shift) of an SO$_2$R group in a 1,3-dipole.

The correctness of the conclusion regarding the structures of the products of thermolysis of IV is confirmed by the data from the IR spectra (see above) and the PMR spectrum of IVa (three signals of NH protons at 7.87, 8.70, and 9.12 ppm) and also by a mass spectroscopic study (see the experimental section).

Compound IVa is dehydrogenated smoothly by chloranil or diethyl azodicarboxylate to give orange diene Va. Its electronic spectrum contains two absorption maxima at 243 (log ε 4.21) and 304 nm (log ε 4.23). According to the PMR spectral data, the signals of both phenyl groups in the spectrum of the product are shifted to weak field as compared with IVa, and this provides evidence for an electron-acceptor group next to them. In addition, only one signal of an NH group at 10.42 ppm is observed. Bands of an NH group at 3244 (m) and 3087 cm^{-1} (w) and of an SO$_2$ group at 1284 (vs) and 1112 cm^{-1} (vs) are observed in the IR spectrum. The compound is easily and quantitatively reduced by tin chloride to starting IVa. Dehydrogenation product Va acquires the acid properties characteristic for a sulfonamide, is quite soluble in alkali, and is methylated by methyl iodide.

To convince ourselves that it was precisely the hydrazino group that underwent dehydrogenation, we carried out the reaction of sulfone Ia with N-methyl-N-phenylhydrazine. In this case we obtained IVd. Bands characteristic for SO$_2$ [1268 (vs) and 1117-1138 (vs)] and NH groups [3278 (s) and 1610 and 1596 cm^{-1} (s)] were observed in its IR spectrum. This substance is not capable of undergoing dehydrogenation by chloranil and diethyl azodicarboxylate. However, oxidation with a solution of potassium ferricyanide gave a reaction product that was identical, according to the analytical and spectral data and its melting point, to the product of dehydrogenation of Va. It is likely that in this case the methyl groups is initially oxidized to a carboxyl group,

TABLE 1. Guanidines IVa-d

Compound	R	R′	Ar	mp, °C	Found, %				Emperical formula	Calc., %				Yield, %
					C	H	N	S		C	H	N	S	
IVa	CH_3	H	C_6H_5	230–232[a]	55,3	5,5	18,3	10,4	$C_{14}H_{16}N_4O_2S$	55,2	5,3	18,5	10,5	33
IVb	C_2H_5	H	C_6H_5	182–183[b]	56,7	5,5	17,7	10,6	$C_{15}H_{18}N_4O_2S$	56,6	5,7	17,6	10,1	35
IVc	CH_3	H	p-ClC_6H_4[c]	214–215[b]	49,6	4,5	16,6		$C_{14}H_{15}ClN_4O_2S$	49,7	4,5	16,6		32
IVd	CH_3	CH_3	C_6H_5	160–161[b]	56,4	6,0	17,5	10,7	$C_{15}H_{18}N_4O_2S$	56,7	5,6	17,6	10,8	40

[a] From dioxane. [b] From alcohol. [c] Found: Cl 10.9%. Calculated: Cl 10.5%.

after which the product undergoes decarboxylation and dehydrogenation.

The structure of IVa was also confirmed by alternative synthesis from the methyl derivative [4] of 1,4-diphenylthiosemicarbazide [5] by reaction with methanesulfonamide sodium salt. The structures of analogs IVb-d were also confirmed by the same prodedure.

The authors sincerely than E. G. Kovalev for his constant interest in this research and for his participation in the discussion of the results.

EXPERIMENTAL*

The electronic spectra of alcohol solutions of the compounds were recorded with a Specord UV spectrophotometer. The IR spectra of mineral oil and perfluorocarbon suspensions of the crystalline compounds were recorded with a UR-20 spectrometer. The PMR spectra of d_6-DMSO solutions of the compounds were recorded with a Perkin–Elmer R-12B spectrometer with hexamethyldisiloxane as the internal standard. The ^{13}C NMR spectra of DMSO solutions were recorded with a Brucker-Physik HX 90 spectrometer. The mass spectra were recorded with a Varian Mat-311 spectrometer. The samples were introduced directly into the ion source of the mass spectrometer at a voltage of 70 eV, an emission current of 300 μA, and an ion-source temperature of 160°. The authors thank N. A. Klyuev for making these measurements.

Guanidines IVa-d (Table 1). A solution of 0.01 mole of 1-aryl-5-alkylsulfonyltetrazole in 0.1 mole of the appropriate arylhydrazine was heated at 170-180° until nitrogen evolution ceased, after which the mixture was cooled and treated with ether, and the precipitate was removed by filtration and washed with ether.

Mass spectrum of IVa [mass number m/e (relative intensity), ion]: 77 (72.1), Ph; 92 (36.9), PhNH; 93 (73.0), $PhNH_2$ migration of hydrogen); 94 (13.8), CH_3SO_2NH; 105 (14.7), PhN = N; 107 (100.0), PhNHNH; 108 (92.8). $PhNHNH_2$ (migration of hydrogen); 119 (70.0), PhN = NCH_2; 197 (4.3), CH_3SO_2N = CNHPh; 209 (2.0), PhNHNHC–NHPh; 225 (27.9), PhNHNHC = N(NHPh); 304 (42.7), M^+.

Alternative Synthesis of IVa. A mixture of 0.005 mole of S-methyldiphenylthiosemicarbazide and 0.005 mole of methanesulfonamide sodium salt, obtained by the addition of an equivalent amount of sodium ethoxide to a solution of methanesulfonamide in absolute alcohol and subsequent separation of the precipitate, in 15 ml of dimethylacetamide was heated on an oil bath at 130° for 3 h, after which it was cooled and poured into ice water (50 ml). The resulting precipitate was removed by filtration and washed with cold water. Recrystallization from alcohol–dioxane gave 0.4 g (26%) of a product with mp 230-232°, which was identical to IVa.

N^1-Methylsulfonyl-N^2-phenyl-C-phenylazoamidine (V). A mixture of 3.04 g (0.01 mole) of IVa and 4.8 g (0.02 mole) of chloranil in 25 ml of xylene was heated at 75-80° fcr 2 h, after which the resulting solution was cooled and filtrated to give 1 g (50%) of an orange product. Crystallization of this product from acetone gave V with mp 142-143°. The product was quite soluble in alcohol and acetone, soluble in hot benzene and carbon tetrachloride, and insoluble in water. The crystalline orange sodium salt formed when the product was dissolved in alkali. Found: C 55.3; H 4.6; N 18.4; S 10.6%. $C_{14}H_{14}N_4O_2S$. Calculated: C 55.6; H 4.7; N 18.5; S 10.6%.

The dehydrogenation of IVa with diethyl azodicarboxylate proceeded similarly (V was obtained in 62% yield).

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*With the participation of A. I. Shadrina.

Methylation of Va. A 0.06-ml (0.001 mole) sample of methyl iodide was added to an alcoholic alkali solution of 0.3 g (0.001 mole) of Va. The next day, the solvent was removed, and the orange solid was removed by filtration and washed with ether to give 0.25 g (80%) of a methylation product with mp 113-115°. Recrystallization from methanol gave a product with mp 120-122°. Found: C 57.3; H 5.1; N 17.7; S 10.1%. $C_{15}H_{16}N_4O_2S$. Calculated: C 57.0; H 5.1; N 17.8; S 10.1%.

Reduction of Va. An alcohol solution of 0.1 g of V was added to an alcoholic hydrogen chloride solution of tin chloride, and the initially colored reaction mixture immediately became colorless. Workup gave 0.1 g of a colorless product with mp 230-232°. No melting-point depression was observed for a mixture of a sample of this product with IVa.

Oxidation of IVd. A solution of 3.0 g (0.009 mole) of potassium ferricyanide in 15 ml of water was added to a suspension of 0.6 g (0.002 mole) of IVd in 35 ml of water, and the mixture was heated to 50-60°, made alkaline, and cooled. It was then acidified, and the orange precipitate was removed by filtration to give 0.5 g (prisms from alcohol) of a product with mp 142-143°. All of the characteristics of the product were identical to those of Va.

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