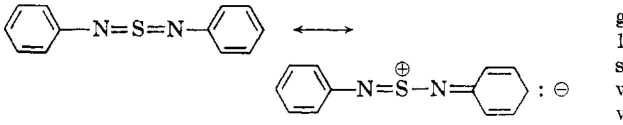
they do not have a similar structural relationship to azobenzene[13] (max. 442 mμ; log ϵ, 2.73).

The color of bis(phenylimino)sulfur may be attributed to resonance forms such as IV.



IV

EXPERIMENTAL

Synthesis of bis(phenylimino)sulfur from phenyliminosulfur difluoride and aniline. A 500-ml. flask fitted with a solid carbon dioxide-cooled condenser, a jacketed dropping funnel, and a magnetic stirrer was charged with 16.1 g. (0.1 mole) phenyliminosulfur difluoride[7] and 100 ml. (liquid) trimethylamine. A solution of 9.3 g. (0.1 mole) aniline in 10 ml. trimethylamine was added during a period of 0.75 hr. from the jacketed dropping funnel. After the mixture had stood at the reflux temperature of trimethylamine for 20 hr., the liquid product was decanted from insoluble trimethylamine hydrofluoride and concentrated at 25° to give 18 g. of red liquid. This material distilled in a molecular still at a pressure of 0.3 mm. when the temperature of the heating block of the still was 97°. As ebullition occurred, this temperature is believed to be the approximate boiling temperature at 0.3 mm. The yield was 15 g. or 70% of theory. The product is a bromine-colored liquid with a density d_4^{25} = 1.190.

Anal. Calcd. for $C_{12}H_{10}N_2S$: S, 14.96; N, 13.08; mol. wt. 214. Found: S, 15.03; N, 13.43; mol. wt. 218.

The infrared spectrum of the liquid was recorded on a Perkin-Elmer model 21 double beam instrument with sodium chloride optics. The electronic spectrum of ethanol solutions of bis(phenylimino)sulfur was measured on a Cary Model 14 double beam spectrophotometer.

From aniline and sulfur tetrafluoride. A solution of 42 g. (0.5 mole) aniline in 125 ml. trimethylamine was stirred at reflux temperature and 27 g. (0.25 mole) gaseous sulfur tetrafluoride[6] was introduced during 1 hr. A moderately exothermic reaction occurred and after 3 hr. the trimethylamine solution was decanted and concentrated at 25°. The residue was distilled through a 6 in. Vigreux column. After 6.4 g. aniline had distilled, 16.0 g. (37% yield) bis(phenylimino)sulfur was collected. It boiled at 114° at 0.8 mm. and had an infrared absorption spectrum identical with the product from phenyliminosulfur difluoride and aniline.

From thionylaniline. A suspension of sodium metal (3.2 g., 0.14 g.-atom) in 3.2 g. toluene was added to a solution of 10 g. (0.1 mole) thionylaniline in 75 ml. toluene and the stirred mixture was heated. At the reflux temperature there was a vigorous reaction which subsided quickly. The mixture was heated 1.5 hr. more, filtered and distilled through a 6 in. Vigreux column. Bis(phenylimino)sulfur distilled at 100°/2 mm. The yield was 2.1 g., 20%. The infrared absorption spectrum was identical with that of the product from phenyliminosulfur difluoride and aniline.

Chemistry of bis(phenylimino)sulfur. Hydrolysis. Samples (0.1 ml.) of bis(phenylimino)sulfur were added to test tubes containing: (1) 0.5 ml. water, (2) 0.5 ml. aqueous 10% sodium hydroxide, (3) 0.5 ml. aqueous 10% hydrogen chloride, (4) 0.4 ml. dioxane + 0.2 ml. water, (5) 0.4 ml. dioxane + 0.2 ml. aqueous 10% sodium hydroxide, and (6) 0.4 ml. dioxane + 0.2 ml. aqueous 10% hydrogen chloride. All of the mixtures initially contained two phases but after 20 hr. almost all the bis(phenylimino)sulfur in solutions 4 and 6 had dissolved and aniline sulfate crystallized from the solution. After 5 days all the mixtures except 1 and 2 had reacted.

Aniline sulfate was identified by comparison of its infrared absorption with an authentic sample.

Bromination. A solution of 1.6 g. (7.5 mmoles) of bis(phenylimino)sulfur in 10 ml. carbon tetrachloride was treated with 5 g. (30 mmoles) of bromine in 20 ml. carbon tetrachloride. A solid, presumably 2,4,6-tribromoaniline hydrobromide, precipitated immediately and after 15 min. was filtered and washed with carbon tetrachloride.

Anal. Calcd. for $C_6N_5NBr_4$: Br, 77.82, S, 0. Found: Br, 75.59, S <0.1. A broad infrared absorption in the range 3.5 to 4.0 μ with peaks at 3.60 μ and 3.92 μ indicates an amine salt.

Acknowledgment. Interpretations of the infrared spectra were made by R. C. Lord of the Massachusetts Institute of Technology and by Naomi E. Schlichter of this laboratory.

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[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Some Aminolysis and Deammonation Reactions of Dialkylsulfamyl Chlorides and Sulfamide with Polyamines

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Reactions of *N*,*N*-disubstituted sulfamyl chlorides and of sulfamide with aliphatic primary and secondary diamines have been employed to prepare sulfamide derivatives of the types $R_2NSO_2NH(CH_2)_nNHSO_2NR_2$ and $H_2NSO_2NH(CH_2)_nNHSO_2NH_2$. Further deammonation to yield a linear polymer of the composition $(—NH(CH_2)_6NHSO_2—)_n$ has been noted when sulfamide and 1,6-hexanediamine are allowed to react under appropriate conditions. The white, crystalline compounds obtained have been characterized in terms of analyses and melting points. Cross-linking in the polymeric material is precluded by the presence of a strong NH stretching absorption at 3280 cm.$^{-1}$ In the aromatic series, the only characterizable product has been obtained from the reaction of *p*-phenylenediamine with *N*,*N*-dimethylsulfamyl chloride.

A number of striking analogies between sulfamide and urea can be distinguished. It might be anticipated, on this basis, that treatment of sulfamide with sufficiently basic amines should lead to deammonation and the formation of various substituted sulfamides. Indeed, several compounds of the general types $RNHSO_2NH_2$, $RNHSO_2NHR$, $R_2NSO_2NH_2$, R_2NSO_2NHR, and $R_2NSO_2NR_2$, where the R-

TABLE I

PROPERTIES AND ANALYSES OF *N*-SUBSTITUTED SULFAMIDES

Compound	Empirical Formula	Yield, %	M.P.[a]	Carbon		Hydrogen		Nitrogen		Sulfur	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1,6-Hexamethylene-*N*,*N'*-bis(dimethylsulfamide)	$C_{10}H_{26}N_4O_4S_2$	60	120–121	36.35	36.28	7.93	7.94	16.96	17.04	—	—
1,4-Cyclohexylene-*N*,*N'*-bis(dimethylsulfamide)	$C_8H_{20}N_4O_4S_2$	50	217–218	32.00	31.99	6.71	6.64	18.66	18.55	—	—
1,4-Benzene-*N*,*N'*-bis(dimethylsulfamide)	$C_{10}H_{18}N_4O_4S_2$	40	233–234	37.26	37.21	5.63	5.49	17.39	17.58	—	—
1,2-Ethane-*N*,*N'*-bis(diethylsulfamide)	$C_{10}H_{26}N_4O_4S_2$	49	52	36.35	36.36	7.93	7.76	16.96	16.73	—	—
1,6-Hexamethylene-*N*,*N'*-bis(diethylsulfamide)	$C_{14}H_{34}N_4O_4S_2$	31	65	43.50	43.24	8.86	8.52	14.50	14.36	—	—
1,4-Cyclohexylene-*N*,*N'*-bis(diethylsulfamide)	$C_{12}H_{28}N_4O_4S_2$	40	107–108	40.44	40.68	7.92	7.73	15.72	15.62	—	—
1,2-Ethane-*N*,*N'*-bis(piperidinesulfamide)	$C_{12}H_{26}N_4O_4S_2$	35	128–129	40.67	40.82	7.39	7.34	15.81	15.51	—	—
1,6-Hexamethylene-*N*,*N'*-bis(piperidinesulfamide)	$C_{16}H_{34}N_4O_4S_2$	49	105–106	46.81	46.70	8.35	8.25	13.65	13.48	—	—
1,4-Cyclohexylene-*N*,*N'*-bis(piperidinesulfamide)	$C_{14}H_{28}N_4O_4S_2$	48	241–242	44.19	44.36	7.42	7.26	14.73	14.92	—	—
1,2-Ethane-*N*,*N'*-bis(morpholinesulfamide)	$C_{10}H_{22}N_4O_6S_2$	35	130–131	33.51	33.65	6.18	6.06	15.63	15.63	—	—
1,6-Hexamethylene-*N*,*N'*-bis(morpholinesulfamide)	$C_{14}H_{30}N_4O_6S_2$	40	119–120	40.55	40.40	7.29	7.31	13.52	13.46	—	—
1,4-Cyclohexylene-*N*,*N'*-bis(morpholinesulfamide)	$C_{12}H_{24}N_4O_6S_2$	56	255–256	37.49	37.70	6.29	6.28	14.58	14.76	—	—
N,*N'*-(Sulfamido)hexamethylenediamine	$C_6H_{18}N_4O_4S_2$	50	157	26.27	26.53	6.61	6.60	20.43	20.05	—	—
N,*N'*-Bis(sulfamido)piperazine	$C_4H_{12}N_4O_4S_2$	50	241–243	12.67	19.69	4.95	4.99	22.95	22.68	—	—
Poly-*N*-hexamethylenesulfamide	$C_6H_{14}N_2O_2S$	—	236–238	40.43	39.85	7.92	8.12	15.72	16.46	17.99	17.33

[a] Uncorrected.

groups in the multi-substituted derivatives may be the same or different, have been obtained readily by this means.[1] However, the unavailability of pure sulfamide has apparently limited the total number and variety of compounds so obtained, and it has proved more convenient to obtain those containing an R_2N-SO_2—group by the ammonolysis or aminolysis of the corresponding disubstituted sulfamyl chlorides.[2,3] Comparatively little is known about analogous deammonation or aminolysis reactions involving diamines. A single reference[4] describes the preparation of 1,2-bis[(dimethylsulfamyl)amino] ethane by the reaction of dimethylsulfamyl chloride with ethylenediamine in benzene.

It has been of interest, therefore, to investigate such reactions and to isolate and characterize the products. Treatment of sulfamide or sulfamyl chlorides with an aliphatic diamine might reasonably affect either one or both of the nitrogen atoms of the amine and lead to mono- or disubstituted derivatives of the types $H_2NSO_2NH(CH_2)_nNH_2$, $H_2NSO_2NH(CH_2)_nNHSO_2NH_2$, $R_2NSO_2NH(CH_2)_n$-NH_2, or $R_2NSO_2NH(CH_2)_nNHSO_2NR_2$. However, under all of the reaction conditions employed, only di-substituted derivatives of the amines were obtained, suggesting that the rate of sulfamylation or deammonation is the same for both nitrogen atoms.

The deammonation and aminolysis reactions studied were limited to those involving sulfamide and dimethyl-, diethyl-, cyclopentamethylene-, and morpholinesulfamyl chlorides. Deammonation was effected by heating a mixture of sulfamide and polyamine in the absence of a solvent. Monomeric derivatives were obtained at 90° with a mole ratio of sulfamide to diamine of 2 to 1. A single polymer, $[\text{—NH(CH}_2)_6\text{NHSO}_2\text{—}]_n$, was prepared upon prolonged heating at 90–120°, using sulfamide and 1,6-hexanediamine in a 1:1 mole ratio. Aminolysis was carried out by refluxing the diamine and the sulfamyl chloride in an inert solvent such as chloroform, benzene, or ethanol. Each polyamine required a specific solvent for optimum results. In every instance, reaction was less readily carried out than with the analogous monoamine, and the yield was correspondingly lower.[3]

The compounds prepared, together with important data relating to their syntheses and properties, are summarized in Table I. All the monomeric compounds are white, crystalline solids that are insoluble in cold water and difficultly soluble in cold organic solvents. Recrystallization can be effected from ethanol, carbon tetrachloride, or water, but not without decomposition. The polymeric hexanediamine derivative is insoluble in hot or cold water

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and in most organic solvents. It does dissolve in *m*-cresol and boiling *N*,*N*-dimethylformamide. Recrystallization is best effected from the latter.

The infrared spectrum of a Nujol mull of the polymer shows absorptions in the 1140–1145 cm.$^{-1}$ and 1320–1340 cm.$^{-1}$ regions. These are due, respectively, to the symmetric and antisymmetric vibrations within the —SO_2— group.[3,5,6] An intense absorption at 3280 cm.$^{-1}$ is due to NH stretching. Thus the possibility of cross-linking is precluded, and the polymer is indicated to be linear.

EXPERIMENTAL

Sulfamide. Sulfamide was prepared as described by Goehring and co-workers.[7] The product was obtained in good purity but in low yields.

Sulfamyl chlorides. Dimethylsulfamyl chloride was prepared according to the procedure of Behrend.[8] The diethyl derivative was synthesized as described by Binkley and Degering.[9] *N*-Pentamethylene sulfamyl chloride was prepared by Denivelle's procedure,[10] as modified by Audrieth and von Brauchitsch.[11] The morpholine derivative, previously known as the product of the reaction between *N*-morpholino chloroamine and sulfur dioxide,[12] was obtained for the first time as follows:

A 67.48-g. sample (0.5 mole) of sulfuryl chloride was placed in a three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a small dropping funnel. The flask was surrounded with an ice-salt bath, and 43.56 g. (0.5 mole) of morpholine was added dropwise with vigorous agitation. The mixture was then refluxed for 12 hr., after which time a clear, red oil was obtained. This was washed several times with a cold solution of sodium carbonate and then extracted with toluene. The resulting solution was dried over calcium chloride and freed of toluene by evaporation under reduced pressure. Vacuum distillation then gave the pure product as a colorless oil boiling at 76° (0.3 mm.), n_D^{20} 1.4910 (lit.[12] n_D 1.4931). Yield: 50.0 g. (54%).

Anal. Calcd. for $C_4H_8NO_3SCl$: C, 25.88; H, 4.34; N, 7.54. Found: C, 25.99; H, 4.46; N, 7.50.

N-Substituted sulfamides. Inasmuch as the procedure followed in each aminolysis or deammonation reaction was essentially the same, only typical syntheses are described in detail. A specific solvent was found to be most effective for each aminolysis reaction, namely chloroform for reactions with ethylenediamine and *p*-phenylenediamine, benzene for reactions with 1,6-hexanediamine, and ethanol for reactions with piperazine.

1,6-Hexamethylene-N,N'-bis(dimethylsulfamide). A 14.35-g. sample (0.1 mole) of dimethylsulfamyl chloride, 11.6 g. (0.1 mole) of 1,6-hexanediamine, and 100 ml. of benzene were placed in a flask equipped with a reflux condenser. The exothermic reaction began immediately. After 1 hr., the mixture was heated to boiling and then refluxed for 2 hr. The resulting hydrochloride was removed by filtration and the residue washed several times with benzene. The solvent was removed *in vacuo*. The resulting dark-colored residue was washed with water and dried. Recrystallization was effected from ethanol.

N,N'-Bis(sulfamido)-1,6-hexamethylenediamine. Two and nine-tenths grams (0.025 mole) of 1,6-hexanediamine and 4.8 g. (0.05 mole) of sulfamide were mixed in a 100-ml. flask equipped with a reflux condenser. The mixture was then heated at 90° by means of an oil bath. The initially rapid evolution of ammonia was complete after 2 hr. The white solid remaining was washed several times with water to remove unchanged sulfamide or polyamine. The product was then obtained by repeated recrystallization from water or ethanol.

Poly-N-hexamethylenesulfamide. Five and eight-tenths grams (0.05 mole) of 1,6-hexanediamine and 4.8 g. (0.05 mole) of sulfamide were placed in a flask fitted with a reflux condenser. The mixture was heated to 90°, at which temperature ammonia was evolved rapidly. The temperature was then increased slowly to 120° and maintained at that level for 6 hr. The tough solid in the cooled flask was removed and ground to a fine white powder. Some ammonia was evolved during grinding. The crude product was then extracted with water in a Soxhlet for 48 hr. and recrystallized from boiling *N*,*N*-dimethylformamide.

Infrared spectra. These were measured with a Perkin-Elmer Model 21 instrument, using a sodium chloride prism.

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