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

Hydrazides of Sulfuric Acid and Their Derivatives.
II. The Sulfamyl Hydrazides[1,2]

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Hydrazinolysis of N-disubstituted sulfamyl chlorides, R_2NSO_2Cl, leads to formation of 4,4-dialkylsulfamyl hydrazides, $R_2NSO_2N_2H_3$, where $R = CH_3$, C_2H_5, and $n\text{-}C_3H_7$, and $R_2N = C_5H_{10}N$ (from piperidine). The sulfamyl hydrazides react with benzoyl chloride, benzenesulfonyl chloride, and with excess sulfamyl chloride to give crystalline products which may be designated as 1-dialkylsulfamyl-2-benzoyl hydrazines (where $R_2N = C_5H_{10}N$), 1-dialkylsulfamyl-2-benzenesulfonyl hydrazines [where $R_2N = (CH_3)_2N$, $(C_2H_5)_2N$, $(n\text{-}C_3H_7)_2N$, and $C_5H_{10}N$] and 1,2-bis(dialkylsulfamyl) hydrazines [where $R_2N = (CH_3)_2N$], respectively. Each of the sulfamyl hydrazides has further been characterized by reaction with typical aldehydes and ketones to form the 4,4-dialkylsulfamyl hydrazones, $R_2NSO_2NHN{=}CHR(CRR')$. Acetylacetone and acetoacetic ester do not yield cyclic products, but react to give a di- and mono-hydrazone, respectively, with N-pentamethylenesulfamyl hydrazide.

We have found it convenient in our earlier studies dealing with the aquo ammono sulfuric acid derivatives[3] such as sulfamic acid, sulfamide, sulfimide, etc., to emphasize certain similarities between these substances and the corresponding aquo ammono carbonic acids, *i.e.*, carbamic acid, urea, cyanic acid, etc. In many instances, methods of preparation are quite similar since they entail processes of solvolysis, solvation, and desolvation. More significant, however, is the fact that the reactions of the two classes of compounds are also very much alike, especially since characteristic chemical properties depend more upon the attached nitrogen-containing groups than they do upon the central elements, namely carbon and sulfur. In the same fashion rather definite analogies can be drawn between (a) the hydrazine derivatives of carbonic acid, such as carbazic acid and carbohydrazide, and (b) the solvo acids of the hydrazine system of compounds derived from sulfuric acid, for example, hydrazinosulfuric acid and sulfuryl dihydrazide.[4] Information with respect to these classes of substances has, however, not been developed adequately, even though both $N_2H_3SO_3H$ and $SO_2(N_2H_3)_2$ have been isolated and characterized. Less well known is sulfamyl hydrazide, $NH_2SO_2N_2H_3$, whose probable formation by reduction of nitrosulfamide has been reported by Ephraim.[5] This substance might be expected to resemble semicarbazide, a carbonic acid derivative related to both the ammonia and hydrazine systems of compounds as a mixed solvo acid.

Attempts have been made in this laboratory to synthesize the parent substance, sulfamyl hydrazide, with little success. It has, however, been possible to prepare 4,4-dialkyl substituted sulfamyl hydrazides and to characterize this new group

$$\begin{array}{c} H_2N{-}NHSO_2NR_2 \\ 1 \quad 2 \quad 3 \quad 4 \end{array}$$

of compounds as typical hydrazides by reaction with aldehydes and ketones and by preparation of some 1-substituted acyl, benzenesulfonyl, and sulfamyl derivatives. Rather than to use a method entailing reduction of sulfamyl nitramines, $R_2NSO_2\text{-}NHNO_2$, as a possible synthetic route, we have found it more convenient to prepare the sulfamyl chlorides and to subject these substances to hydrazinolysis.

$$R_2NSO_2Cl + 2\ N_2H_4 \rightarrow R_2NSO_2N_2H_3 + N_2H_4{\cdot}HCl$$
$$(\text{where } R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7)$$

The 4,4-dialkylsulfamyl hydrazides are relatively unstable, low-melting compounds. They undergo hydrolysis in aqueous solution, especially in acidic media, thus furnishing further evidence for the instability of the S—N linkage toward acid hydrolysis observed previously for hydrazinosulfuric acid.[6] Based upon qualitative observations, hydrolysis and decomposition appear to proceed concurrently, probably in accordance with the following equations:

$$R_2NSO_2N_2H_3 + H_2O \xrightarrow{H^+} \underline{R_2NSO_2OH} + \underline{N_2H_4{\cdot}H^+}$$
$$R_2NSO_2N_2H_3 \rightarrow \underline{R_2NH{\cdot}H^+} + \underline{SO_2} + N_2 + H_2.$$

Products underlined in the above equations have been isolated and identified.

If an excess of sulfamyl chloride is allowed to react with hydrazine, "sulfamylation" occurs on both nitrogen atoms of the hydrazine molecule to yield compounds which may be designated as 1,2-bis(dialkylsulfamyl) hydrazines, $[{-}NHSO_2NR_2]_2$. Reaction of the sulfamyl hydrazides with benzoyl chloride and with benzenesulfonyl chloride leads to

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(1) For the first article of this series see reference (6).

(2) This investigation was carried out under the sponsorship of the Office of Ordnance Research as one phase of a fundamental study of the chemistry of hydrazine, Contract No. DA-11-022-ORD-828.

(3) Audrieth, Sveda, Sisler, and Butler, *Chem. Revs.*, **26**, 49 (1940).

(4) Audrieth and Ogg, *The Chemistry of Hydrazine*, John Wiley and Sons, New York, New York, 1951, Chapter XI.

(5) Ephraim and Piotrowski, *Ber.*, **44**, 397 (1911).

(6) Audrieth and West, *J. Am. Chem. Soc.*, **77**, 5000 (1955).

well-defined crystalline products which may be designated as 1-dialkylsulfamyl-2-benzoyl (or benzenesulfonyl) hydrazines. Characteristic aldehyde and ketone derivatives of the sulfamyl hydrazides have also been prepared and may be designated as dialkylsulfamyl *hydrazones* or as *1-alkylidene (arylidene)-4-dialkylsulfamyl hydrazides.*

The present investigation constitutes an exploratory study of this new and interesting class of compounds. The preparation of the sulfamyl hydrazides and of their derivatives is depicted in outline form in Figure 1.

EXPERIMENTAL[7]

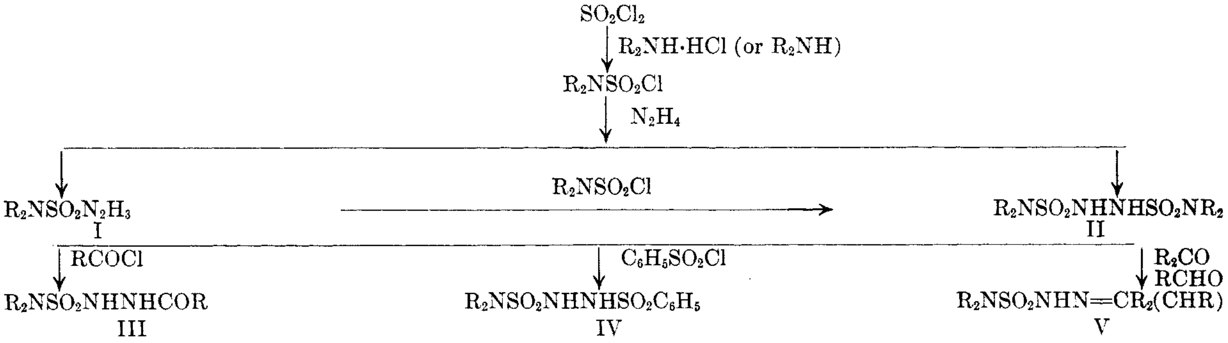

FIG. 1. SOME DERIVATIVES OF THE SULFAMYL HYDRAZIDES

(I) 4,4-Dialkylsulfamyl hydrazides
(II) 1,2-Bis(dialkylsulfamyl) hydrazine
(III) 1-Dialkylsulfamyl-2-acyl hydrazine
(IV) 1-Dialkylsulfamyl-2-benzenesulfonyl hydrazine
(V) 1-Alkylidene(arylidene)-4,4-dialkylsulfamyl hydrazides

Sulfamyl chlorides. Dimethylsulfamyl chloride was prepared from sulfuryl chloride and dimethylamine hydrochloride according to the method of Behrend;[8] the diethyl- and di-*n*-propyl- derivatives were obtained by an analogous procedure.[9] The procedure described by Denivelle[10] for the synthesis of the piperidino derivative, N-pentamethylenesulfamyl chloride, was modified as follows:

To a solution of 70 g. sulfuryl chloride (0.5 mole) in 150 ml. of toluene cooled in an ice-salt bath there was added dropwise with vigorous agitation 85 g. piperidine (1.0 mole) at such a rate that the temperature of the reaction mixture was maintained below 0°. Then 25 ml. of water was added and the mixture was allowed to warm to room temperature. The toluene layer was separated from the aqueous layer and was washed successively with water, with 10% hydrochloric acid to remove unreacted piperidine, with sodium bicarbonate solution, and finally again with water, after which time the solution was dried over Na_2SO_4. The excess toluene was first removed by distillation and the residue was fractionated under reduced pressure to give 37 g. (40%) of N-pentamethylenesulfamyl chloride, b.p. 112°/5 mm.

Sulfamyl hydrazides. Hydrazinolysis of the sulfamyl chlorides was effected by adding a solution of the sulfamyl chloride in anhydrous ether to a suspension of hydrazine in ether. The procedure is illustrated by the following example:

N-Pentamethylenesulfamyl chloride (53 g., 0.3 mole) was dissolved in 100 ml. of anhydrous ether and added dropwise and with vigorous agitation to a suspension of 20 g. (0.6 mole) of hydrazine (95%) in 100 ml. of anhydrous ether cooled in an ice-bath. The mixture was allowed to warm to room temperature and stirring was continued for one hour. The lower liquid layer then was separated and extracted three times with 75 ml. of ether. The ether layer and the ether extracts were concentrated to about 150 ml. and cooled to −10°. The crystals of N-pentamethylenesulfamyl hydrazide were removed by filtration and were purified by recrystallization from ether. Yield, 12 g. (19%).

The 4,4-diethyl- and 4,4-dimethyl-sulfamyl hydrazides were prepared and isolated by essentially the same procedure. However, the 4,4-di-*n*-propyl derivative could not be recovered from the reaction mixture because of its high solubility in ether. Crystallization of the hydrazide was accomplished by concentration of the ether layer and extracted to about 30 ml. followed by the addition of 200 ml. of petroleum ether and cooling to −10°.

Product yields of the various sulfamyl hydrazides were not too satisfactory, varying from 10 to 20% of theory. Melting points and analytical data for some 4,4-dialkylsulfamyl hydrazides are given in Table I.

1-Dialkylsulfamyl-2-benzenesulfonyl hydrazines. A solution of 0.01 mole of the 4,4-dialkylsulfamyl hydrazide in 3 to 5 ml. of anhydrous ether was added to 0.01 mole of benzenesulfonyl chloride in 2 ml. of pyridine. The desired compounds were found to separate as oils. These first were washed with petroleum ether and then with water to remove pyridine hydrochloride and to bring about solidification. Recrystallization was generally effected from a benzene-petroleum ether solvent mixture. Melting points and analytical data of some typical 1-dialkylsulfamyl-2-benzenesulfonyl hydrazines are given in Table II.

1-N-Pentamethylenesulfamyl-2-benzoyl hydrazine. This procedure gives an illustration of the preparation of a typical acyl derivative. The sulfamyl hydrazide (1.8 g.) in 5 ml. of ethanol was added to 2.8 g. of benzoyl chloride in 2 ml. of pyridine. The resulting mixture was cooled to effect crystallization of the product, which was purified by recrystallization from ethanol, m.p., 195°.

Anal. Calc'd for $C_{12}H_{17}O_3N_3S$: C, 50.9; H, 6.1; N, 14.8. Found: C, 51.0; H, 6.1; N, 15.1.

Reaction with aldehydes and ketones. Equimolar quantities of the sulfamyl hydrazide and the desired aldehyde or ketone were allowed to react in ether solution. After warming the reaction mixture for about an hour the solvent was removed by evaporation to yield a solid product which was recrystallized from benzene-petroleum ether for purification. Melting points and analytical data for a number of 4,4-dialkylsulfamyl hydrazones are summarized in Table III.

The reactions of N-pentamethylenesulfamyl hydrazide with acetoacetic ester and with acetylacetone did not result

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[7] All melting points are uncorrected.

[8] Behrend, *Ann.*, **222**, 116 (1884).

[9] Binkley and Degering, *J. Am. Chem. Soc.*, **61**, 3250 (1939).

[10] Denivelle, *Bull. soc. chim. France*, [5] **3**, 2143 (1936).

TABLE I

4,4-DIALKYLSULFAMYL HYDRAZIDES

($R_2N{\cdot}SO_2NH{\cdot}NH_2$)

					Analytical Data			
			Carbon		Hydrogen		Nitrogen	
R_2N—	M.P., °C.	Empirical Formula	Calc'd	Found	Calc'd	Found	Calc'd	Found
$(CH_3)_2N$—[a]	15–17	$C_2H_9N_3O_2S$	—	—	—	—	—	—
$(C_2H_5)_2N$—	40–42	$C_4H_{13}N_3O_2S$	28.7	28.1	7.8	7.8	25.1	25.2
$(n\text{-}C_3H_7)_2N$—	41	$C_6H_{17}N_3O_2S$	36.9	37.0	8.7	8.6	21.5	21.6
$CH_2(CH_2)_3CH_2N$—	60	$C_5H_{13}N_3O_2S$	33.5	33.9	7.3	7.4	23.5	23.7

[a] The identity of 4,4-dimethylsulfamyl hydrazide was established by preparation of a series of aldehyde and ketone derivatives. Its low melting point and instability made analysis and characterization difficult.

TABLE II

1-DIALKYLSULFAMYL-2-BENZENESULFONYL HYDRAZINES

($R_2N{\cdot}SO_2NH{\cdot}NH{\cdot}SO_2C_6H_5$)

					Analytical Data			
			Carbon		Hydrogen		Nitrogen	
R_2N—	M.P., °C.	Empirical Formula	Calc'd	Found	Calc'd	Found	Calc'd	Found
$(CH_3)_2N$—	141	$C_8H_{13}N_3O_4S_2$	34.4	34.4	4.7	4.9	15.0	14.9
$(C_2H_5)_2N$—	118	$C_{10}H_{17}N_3O_4S_2$	39.1	40.4	5.6	5.6	13.7	13.2
$(n\text{-}C_3H_7)_2N$—	116	$C_{12}H_{21}N_3O_4S_2$	43.0	42.5	6.3	6.2	12.5	12.6
$C_5H_{10}N$—	137	$C_{11}H_{17}N_3O_4S_2$	41.4	41.3	5.4	5.2	13.2	13.0

TABLE III

4,4-DIALKYLSULFAMYL HYDRAZONES

[$R_2N{\cdot}SO_2NH{\cdot}N{=}CRR'(CHR)$]

[1-ALKYLIDENE(ARYLIDENE)-4,4-DIALKYLSULFAMYL HYDRAZIDES]

						Analytical Data			
				Carbon		Hydrogen		Nitrogen	
R_2N—	CRR′	Empirical Formula	M.P., °C.	Calc'd	Found	Calc'd	Found	Calc'd	Found
$(CH_3)_2N$—	CHC_6H_5	$C_9H_{13}N_3O_2S$	104	47.6	47.4	5.8	5.3	18.5	18.7
	$o\text{-}CHC_6H_4OH$	$C_9H_{13}N_3O_3S$	114	44.4	44.6	5.4	5.5	17.3	17.8
	$C(CH_3)_2$	$C_5H_{13}N_3O_2S$	68	33.5	33.1	7.3	7.3	23.5	23.7
	$C(CH_3)(C_6H_5)$	$C_{10}H_{15}N_3O_2S$	102	49.8	48.7	6.3	6.1	17.4	17.3
$(C_2H_5)_2N$—	CHC_6H_5	$C_{11}H_{17}N_3O_2S$	80	51.8	51.1	6.7	6.6	16.5	16.5
	$o\text{-}CHC_6H_4OH$	$C_{11}H_{17}N_3O_3S$	108	48.7	48.8	6.3	6.4	15.5	15.4
	$C(CH_3)_2$	$C_7H_{17}N_3O_2S$	50	40.6	40.4	8.3	8.2	20.3	20.4
$(n\text{-}C_3H_7)_2N$—	$o\text{-}CHC_6H_4OH$	$C_{13}H_{21}N_3O_3S$	107	52.1	52.2	7.1	7.2	14.0	14.3
$C_5H_{10}N$—	CHC_6H_5	$C_{12}H_{17}N_3O_2S$	132	53.9	54.3	6.4	6.5	15.7	15.6
	$o\text{-}CHC_6H_4OH$	$C_{12}H_{17}N_3O_3S$	138	50.9	51.4	6.1	5.9	14.8	15.0
	$C(CH_3)_2$	$C_8H_{17}N_3O_2S$	108	43.8	44.2	7.8	7.6	19.2	18.7
	$C(CH_3)(C_6H_5)$	$C_{13}H_{19}N_3O_2S$	127	55.5	55.8	6.8	6.8	—	—
	$C(C_6H_5)_2$	$C_{18}H_{21}N_3O_2S$	173	63.0	62.1	6.2	6.2	12.2	12.5
	$C{-}(CH_2)_4CH_2$	$C_{11}H_{21}N_3O_2S$	114	50.9	51.2	8.2	8.1	16.2	16.0
	$[C(CH_3)CH_2(CH_3)C]$[a]	$C_{15}H_{30}N_6O_4S$	164	42.6	43.4	7.2	7.1	19.9	19.8
	$[C(CH_3)(CH_2COOC_2H_5)]$[b]	$C_{11}H_{21}N_3O_4S$	72	45.3	45.6	7.3	7.4	14.4	15.2

[a] $CH_2[CH_3C({=}NNHSO_2NC_5H_{10})]_2$ was prepared from acetylacetone. [b] $CH_3C({=}NNHSO_2NC_5H_{10})CH_2COOC_2H_5$ was prepared from acetoacetic ester.

in the formation of cyclic products. Analytical data were found to correspond to formation of the sulfamyl hydrazones.

1,2-Bis(dimethylsulfamyl)hydrazine.[11] To a solution of 15 g. (0.1 mole) of 4,4-dimethylsulfamyl chloride in anhydrous ether there was added 3.2 g. (0.1 mole) of hydrazine. After stirring for one hour the ether layer was separated from the unreacted hydrazine and concentrated to yield an oily liquid which crystallized very slowly on standing. The product was purified by recrystallization from absolute ethanol; m.p., 110°. Yield, 3 g. (24%).

Anal. Calc'd for $C_4H_{14}N_4O_4S_2$: C, 19.5; H, 5.7; N, 22.8. Found: C, 20.0; H, 5.6; N, 22.7.

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(11) There is evidence that the 1,2-bis(dialkylsulfamyl) hydrazines are obtained as by-products during the preparation of the 4,4-dialkylsulfamyl hydrazides. The ether solution remaining after removal of the desired product in the synthesis of 4,4-diethylsulfamyl hydrazide was found on further treatment to contain a crystalline product melting at 115° whose composition approached that required for the 1,2-bis(diethylsulfamyl)hydrazine.