[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL RESEARCH LABORATORIES OF THE FIRESTONE TIRE AND RUBBER COMPANY]

REACTIONS OF MONO- AND DI-AMINES WITH CARBON DISULFIDE. I. N,N'-DIALKYLETHYLENEDIAMINE-CARBON DISULFIDE REACTIONS[1]

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The literature is replete with reactions of dialkylmonoamines and carbon disulfide; the products are dialkylammonium salts of dialkyldithiocarbamic acids (I) and may be oxidized to thiuram disulfides (II). These compounds are used widely in the rubber industry as vulcanization accelerators. More recently Smith, Alliger, Carr, and Young (1) of this laboratory have shown that, under certain conditions, the oxidation of dialkyldithiocarbamates in the presence of primary or secondary amines may produce thiocarbamylsulfenamides (III). The decomposition of this type of compound by loss of sulfur results in an N,N'-disubstituted thiourea (IV).

However, analogous reactions of N,N'-dialkyldiamines with carbon disulfide have received only scant attention and the purpose of this investigation was to study this field of chemistry.

It was found that, in general, the reactions of N,N'-dialkylethylenediamines with carbon disulfide follow the same pattern as similar reactions in the dialkylmonoamine series. However, in the diamine series the products are cyclic by virtue of the ethylene chain which links the nitrogen atoms. The analogies between reactions of mono- and di-amines with carbon disulfide are summarized in Chart I; compounds possessing related structures bear the same number with the "A" series representing the cyclic types.

The reaction of ethylenediamine and carbon disulfide was first reported by Hofmann (2) who obtained a product shown to be N-(β-aminoethyl)dithiocarbamic acid (I-A, R = H). He thermally decomposed this acid and obtained hydrogen sulfide and 2-imidazolidinethione (IV-A, R = H). Subsequently these reactions were extended to N-substituted ethylenediamines by Ristenpart (3), Lob (4), van Alphen (5), Sebrell and Clifford, (6, 7), Zienty and Thielke (8), Zienty (9), Newman (10), and Schinzel and Benoit (11).

Using similar reactions we have prepared other 1,3-dialkyl-2-imidazolidinethiones from the thermal decomposition of the corresponding N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acid inner salts (I-A). Furthermore, it was found that the dithiocarbamic acid inner salts could be oxidized to a new type of compound, the tetrahydro-1,2,5-thiadiazine-6-thiones (III-A), and these new compounds likewise could be thermally decomposed to the same 2-imidazolidinethiones. The new heterocyclic compounds, the tetrahydro-1,2,5-thiadiazines, may be considered to be cyclic thiocarbamylsulfenamides, and their mode of

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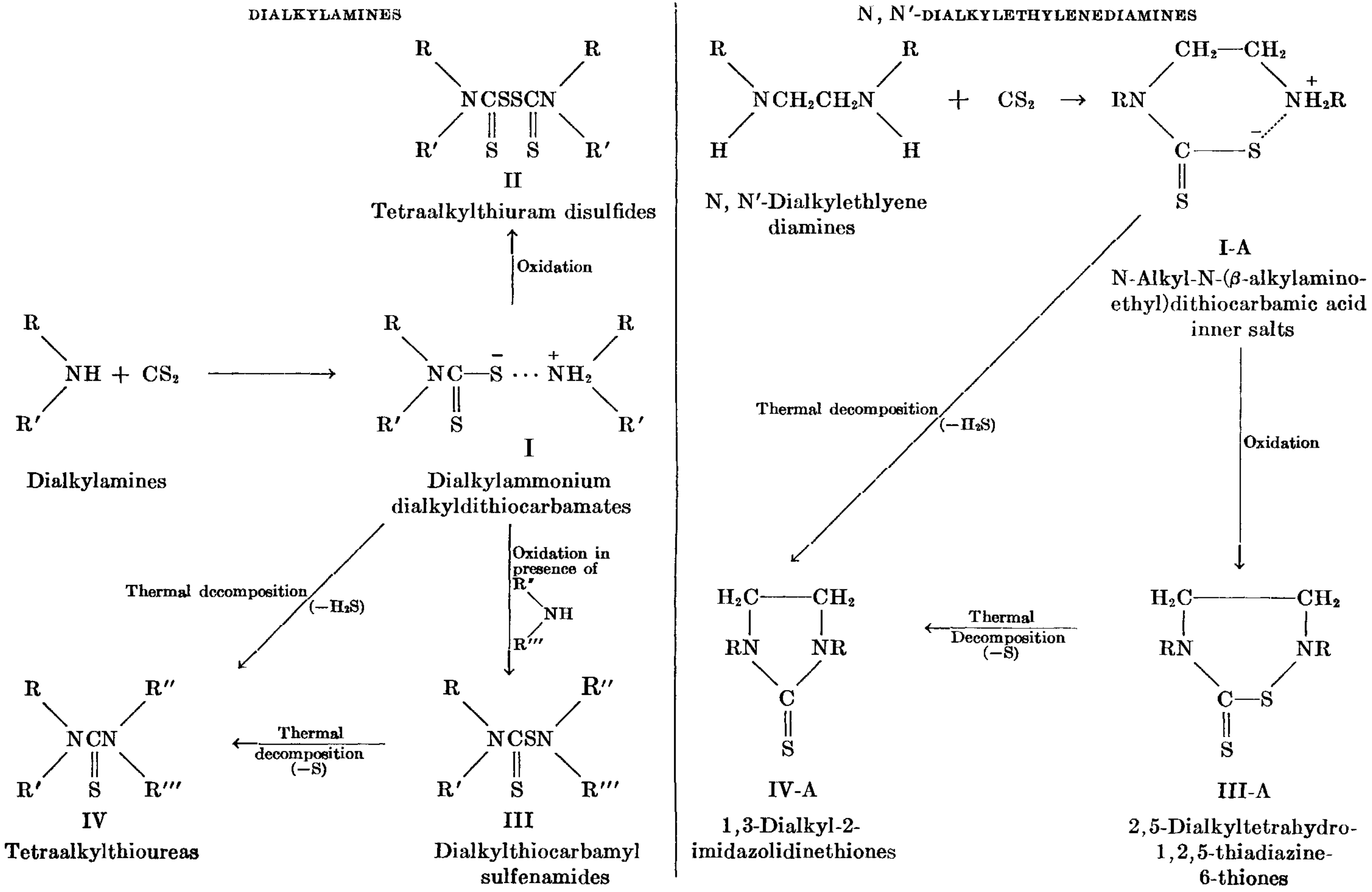
CHART I

Summary of amine-Carbon Disulfide Reactions



formation is analogous to the formation of the open chain thiocarbamylsulfenamides (III) from the dialkylammonium dithiocarbamates (I) (1). Fisher-Hirschfelder-Taylor models show that the six-membered thiadiazine ring is strain-free, but lacks some of the symmetry and stability of the five-membered imidazolidine ring.

It is interesting to note that by analogy with the oxidation of the dialkyldithiocarbamates, the oxidation of the β-alkylaminoethyldithiocarbamic acid inner salts (I-A) could have taken either one of two courses, namely, (a) the formation of a thiuram disulfide from two molecules of acid inner salt or, (b) the intramolecular oxidation to a cyclic thiocarbamylsulfenamide. The latter was a possibility because of the proximity of the mercapto and β-amino groups in the same molecule. The molecular weight values of the products from iodine oxidation of the inner salts indicated that reaction (b) occurred in preference to reaction (a). Analogous to the loss of hydrogen sulfide on thermal decomposition of the dithiocarbamic acid inner salts (I-A), their oxidation products, the tetrahydro-1,2,5-thiadiazine-6-thiones (III-A) readily decomposed with the loss of the ring sulfur leaving 2-imidazolidinethiones (IV-A). The stability of the tetrahydrothiadiazine ring appeared to be related to the size of the alkyl substituent, R. If R was cyclohexyl, the compound could be stored for several weeks without decomposition. However, when R was isopropyl, the pure white compound developed a yellow coloration within several days, probably caused by the formation of free sulfur. Attempts to prepare the ethyl substituted compound resulted chiefly in IV-A and sulfur; only a low yield of the desired thiadiazine product was obtained.

In the monoamine series, the thiocarbamylsulfenamides decompose thermally in an analogous manner to yield substituted thioureas (1). The thermal decomposition of substituted ammonium dithiocarbamates also is assumed to give the same substituted thioureas, although this has been reported only for a dithiocarbamate from a primary amine (13).

EXPERIMENTAL

Preparation of N,N′-dialkylethylenediamines. The N,N-dialkylethylenediamines were prepared by the reaction of ethylene dichloride with primary amines. The alkyl substituents were ethyl, isopropyl, *n*-butyl, *sec*-amyl, cyclohexyl, and 2-ethylhexyl. These diamines were colorless to slightly yellow liquids and all except the *sec*-amyl and 2-ethylhexyl compounds rapidly absorbed water from the air to form solid hydrates.

The general procedure was the same in each case and the preparation of the butyl derivative is given as an example: A mixture of 1.5 moles of ethylene dichloride and 6.6 moles of *n*-butylamine in a 1200-ml. steel bomb was heated electrically. At 104° the temperature suddenly rose to 204°. After cooling, the reaction product, a mushy liquid, was made alkaline with 40% aqueous sodium hydroxide solution, filtered, and the organic layer in the filtrate distilled through a 6-inch Vigreux column. After recovery of excess butylamine the desired product distilled at 92°/4 mm.; yield, 130 g. (50%).

Reactions between ethylene dichloride and amines boiling above 90° were performed in a round-bottom flask equipped with stirrer, reflux condenser, and dropping-funnel. The dichloride was added slowly to the amine at 90–120°. The product was recovered from the reaction mixture as described above.

The N,N′-dialkylethylenediamines which were highly water-soluble, *e.g.*, the diethyl

TABLE I

N,N'DIALKYLETHYLENEDIAMINES, THEIR CARBON DISULFIDE REACTION PRODUCTS, N-ALKYL-N-(β-ALKYLAMINOETHYL)DITHIOCARBAMIC ACIDS (I-A) AND THERMAL DECOMPOSITION PRODUCTS, 1,3-DIALKYL-2-IMIDAZOLIDINETHIONES (IV-A)

R IN FORMULAS I-A, III-A AND IV-A	N,N'-DIALKYLETHYLENEDIAMINE B.P., °C. (UNCORR.)/MM.	DITHIOCARBAMIC ACID (I-A)					1,3-DIALKYL-2-IMIDAZOLIDINETHIONE (IV-A)				
		Decomposition Temperature, °C. (corr.)	ANALYSES				Properties	Analyses			
			Calc'd		Found			Calc'd		Found	
			N	S	N	S		N	S	N	S
Ethyl	150–154/733[b] 65.5/35	157.0–157.4 (white solid)	14.55	33.34	14.7	33.2	m.p., 62.2° (corr.)	17.70	20.26	17.7	20.0
Isopropyl	84/37	153.8–154.4 (white solid)	12.71	29.09	12.8	28.9	m.p. 86.4° (corr.)	15.03	17.20	15.0	17.55
n-Butyl	92/4[c, d]	(white solid)	—	—	—	—	b.p. 144–149°/1[d] n_D^{25} 1.5267	13.07	14.96	13.13	15.18
1-Methylbutyl	86–87/2	(oily viscous liquid)	—	—	—	—	b.p., 149–151°/1 n_D^{25} 1.5203	11.55	13.22	11.65	—
Cyclohexyl	134–136/3[e, f]	166.5–169[e] (white solid)	9.32	21.34	9.7	—	m.p., 226.2° (corr.)[e]	10.51	12.03	10.7	12.6
2-Ethylhexyl	121.5–124/0.5	(oily viscous liquid)	—	—	—	—	b.p., 177–178°/1 n_D^{25} 1.5070	8.58	9.82	8.77	9.69

[a] The sample in a m.p. tube was immersed in a bath approximately 10° below the decomposition temperature. The bath was then heated so that the temperature rose 2° per minute. [b] Schneider (12) reported b.p. 149–150°. [c] Sebrell and Clifford (6) reported b.p. 185–187°/3, probably a misprint in U.S. Patent 1,948,317 (1934). [d] Zienty (9) reported b.p. of diamine, 110–111°/8, decomposition of the acid at 135–136°, and b.p. of 2-imidazolidinethione, 183–184°/8. [e] Zienty and Thielke (8) reported b.p. of diamine 184–186°/25, decomposition of acid at 167–168°, and m.p. of 2-imidazolidinethione, 225–226°. [f] Clifford (7) reported b.p. 136–147°/2.

and diisopropyl derivatives, could be separated from water in improved yields by azeotropic distillation using benzene or toluene as an entrainer (14).

Preparation of N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acid inner salts (I-A). When carbon disulfide was added slowly to the benzene or acetone solutions of the N,N′-dialkylethylenediamines, the highly exothermic formation of the N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acid inner salts (I-A) occurred spontaneously. The amyl- and 2-ethylhexyl-substituted compounds failed to separate from solution; evaporation of the solvent in each case left a viscous yellow-orange oil which did not crystallize. The other acid salts precipitated in the reaction mixture as white powders and three of these were characterized (Table I).

An example is the preparation of the compound in which each of the alkyl groups is isopropyl: A solution of 0.5 mole (72 g.) of N,N′-diisopropylethylenediamine in 500 cc. of acetone was cooled to 10°. This was stirred vigorously while 0.53 mole (40 g.) of carbon disulfide in 40 cc. of acetone was added dropwise. A white precipitate soon formed and external cooling was necessary to keep the temperature below 15°. After complete addition, the precipitate was filtered and washed with acetone and ether. Yield, 96 g. (90%) of a white powder (Table I).

TABLE II

PROPERTIES OF 2,5-DIALKYLTETRAHYDRO-1,2,5-THIADIAZINE-6-THIONES (III-A)

R IN FORMULA (III-A)	M.P., °C. (corr.).	MOLECULAR WEIGHT			ANALYSES			
		Calc'd for Thiuram disulfide	Calc'd for Tetrahydrothiadiazinethione	Found[a]	Calc'd		Found	
					N	S	N	S
Ethyl	62.0–62.5[b]	382.6	190.3	197	14.71	33.69	14.9	33.9
Isopropyl	104.8–105.0	438.8	218.4	214	12.82	29.32	13.2	29.6
Cyclohexyl	138.8–139.6	599.0	298.5	299	9.41	21.48	9.8	21.7

[a] Determined by the cryoscopic method in benzene. [b] Mixture m.p. of this compound with 1,3-diethyl-2-imidazolidinethione (m.p. 62.2°) was 42–50°, thereby establishing the non-identity of the two closely related compounds.

The compounds shown in Table I were insoluble in the usual organic solvents, but could be purified by solution in ammonia water followed by volatilization of the ammonia at room temperature.

Thermal decomposition of N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acids (I-A) to 1,3-dialkyl-2-imidazolidinethiones (IV-A). A few grams of the dithiocarbamic acid inner salt was heated in a test tube to slightly above its decomposition temperature until evolution of hydrogen sulfide ceased. The loss of hydrogen sulfide occurred at a fairly definite temperature that is, about 160–170°, although this varied a few degrees with rate of heating and particle size (Table I). The residue containing the corresponding 2-imidazolidinethione, (IV-A), was recrystallized from acetone, ether, or alcohol to constant melting point. Liquid products (alkyl groups = butyl, amyl, and 2-ethylhexyl) were distilled under reduced pressure.

Oxidation of N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acids (I-A) to 2,5-dialkyltetrahydro-1,2,5-thiadiazine-6-thiones (III-A). Example; R = isopropyl. A solution of 0.4 mole (88 g.) of N-isopropyl-N-(β-isopropylaminoethyl)dithiocarbamic acid in 500 cc. of 1.4 *N* aqueous sodium hydroxide solution was stirred vigorously while aqueous iodine-potassium iodide solution was added dropwise. After precipitation was complete, the product was filtered, dried, and dissolved in acetone. The clear acetone solution was evaporated almost to dryness after which the pale yellow crystals were filtered. Recrystallization from benzene gave 62 g. (71%) of white needles, m.p. 104.8–105.0° (corr.).

Thermal decomposition of 2,5-dialkyltetrahydro-1,2,5-thiadiazine-6-thiones (III-A) to 1,3-dialkyl-2-imidazolidinethiones (IV-A). A few grams of the thiadiazinethione (III-A) in a test tube was heated gently until condensation of sulfur at the mouth of the tube no longer occurred. The residue, containing the corresponding 2-imidazolidinethione, (IV-A), was purified by recrystallization or distillation. Identifications of the products were made by obtaining mixture melting points without lowering, with authentic samples, or by comparing the boiling points and refractive indices of the liquids with those of authentic samples.

SUMMARY

1. A series of N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acid inner salts was prepared from N,N′-dialkylethylenediamines and carbon disulfide. Thermal-decomposition products of these salts were hydrogen sulfide and 1,3-dialkyl-2-imidazolidinethiones.

2. Halogen oxidation of these acids gave a series of new compounds, 2,5-dialkyltetrahydro-1,2,5-thiadiazine-6-thiones. These new heterocyclic compounds decomposed thermally to produce sulfur and 1,3-dialkyl-2-imidazolidinethiones identical to those produced from the dithiocarbamic acid inner salts.

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REFERENCES

(1) SMITH, ALLIGER, CARR, AND YOUNG, *J. Org. Chem.*, preceding paper.
(2) HOFMANN, *Ber.*, **5**, 241 (1875).
(3) RISTENPART, *Ber.*, **29**, 2527 (1896).
(4) LOB, *Rec. trav. chim.*, **55**, 859 (1936).
(5) VAN ALPHEN, *Rec. trav. chim.*, **55**, 412, 669, and 835 (1936); **57**, 265 (1938); **58**, 544 (1939); **59**, 31 (1940).
(6) SEBRELL AND CLIFFORD, U. S. Patent 1,948,317 (Feb. 20, 1934).
(7) CLIFFORD, U. S. Patent 2,126,620 (Aug. 9, 1938).
(8) ZIENTY AND THIELKE, *J. Am. Chem. Soc.*, **67**, 1040 (1945).
(9) ZIENTY, *J. Am. Chem. Soc.*, **68**, 1388 (1946).
(10) NEWMAN, *Ber.*, **24**, 2191 (1891).
(11) SCHINZEL AND BENOIT, *Bull. soc. chim.*, (5) **6**, 501 (1939).
(12) SCHNEIDER, *Ber.*, **28**, 3077 (1895).
(13) FISCHER, *Ann.*, **190**, 118 (1877).
(14) Unpublished work of Dr. L. E. Forman of this laboratory.