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

REACTIONS OF MONO- AND DI-AMINES WITH CARBON DISULFIDE. II. METHYLENEDIAMINE AND IMIDAZOLIDINE-CARBON DISULFIDE REACTIONS[1]

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The analogy between dialkylmonoamine-carbon disulfide and the homologous N,N′-dialkyldiamine-carbon disulfide reactions was discussed in Part I. We will show that a parallelism also is found between the dialkylmonoamine-formaldehyde-carbon disulfide and the N,N′-dialkyldiamine-formaldehyde-carbon disulfide reactions. These have been summarized in Chart I; as in Part I, the compounds with related structures have the same number with the "A" series representing the cyclic types.

Dialkylamine-aldehyde-carbon disulfide products have been patented (1, 2, 3) as accelerators for the vulcanization of rubber, although the patents contain no suggestion of molecular structures of the reaction products.

Three methods are available for the synthesis of amine-aldehyde-carbon disulfide accelerators. For example, we have found that the compound obtained from methylene-*bis*-piperidine (I, R and R′ = cyclopentamethylene) and carbon disulfide is identical with the compound prepared by Levi (4) from piperidinium N,N-cyclopentamethylenedithiocarbamate (III, R and R′ = cyclopentamethylene) and formaldehyde. Furthermore, we have prepared the same compound from the dithiocarbamate (III) and piperidinomethanol. This would indicate that the order of addition of formaldehyde and carbon disulfide to the amine does not affect the nature of the final product.

The third method, which involves the use of an alkylaminomethanol, also makes possible the synthesis of the same type of compound in which the N and N′ alkyl groups are dissimilar. The reaction of piperidinomethanol with morpholinium N,N-oxadiethylenedithiocarbamate and with dicyclohexylammonium N,N-dicyclohexyldithiocarbamate resulted in products having dissimilar N,N′-alkyl substituents. These also were found to have activity in accelerating the vulcanization of rubber.

The structure of the above compounds, which result from the three methods of preparation just described, has not been clearly elucidated. Levi proposed an electrovalent, salt type of structure for his product, namely, methylenepiperidinium N,N-cyclopentamethylenedithiocarbamate (II-alternate, R and R′ = cyclopentamethylene). However, there is also the possibility that the methylene group can act as a purely covalent link between the dithiocarbamic acid and amine radicals thereby forming a dithioester, N′,N′-dialkylaminomethyl N,N-dialkyldithiocarbamate (II). In fact similar compounds have been patented by

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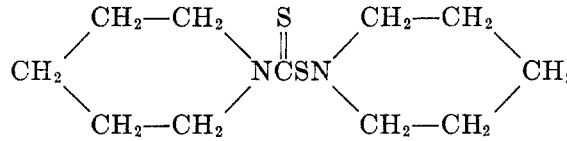
Sloan (5) as vulcanization accelerators but he did not disclose their method of preparation.

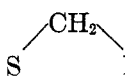
Conclusive chemical evidence for establishing the ester (II) or salt (II-alternate) structure is lacking. However, the physical behavior of this type of compound substantiates the plausibility of II rather than II-alternate. The basis of proposing an ester structure (II) lies in observations on electrical conductivity, solubility, and melting point. The conductivities of 0.01 *M* solutions of three compounds in nitrobenzene were determined[2]; these were II or II-alternate (R and R′ = cyclopentamethylene), III (R and R′ = cyclopentamethylene), and N,N-cyclopentamethylenethiocarbamyl-N′,N′-cyclopentamethylenesulfenamide (Part I, Ref. 1):



III is known to be a salt and should exhibit relatively high conductivity in a solvent of high dielectric constant. On the other hand, the sulfenamide is entirely covalent and its lack of ionization would contribute little to the conductivity of the solution. The conductivity of II or II-alternate should be near that of either III or the sulfenamide. Specific conductances of 0.01 *M* solutions in ohm^{-1} $cm.^{-1}$ at 25° were:

Nitrobenzene	5.5×10^{-9}
Sulfenamide (covalent)	5.5×10^{-9}
III (electrovalent)	18.0×10^{-9}
II or II-alternate	6.6×10^{-9}

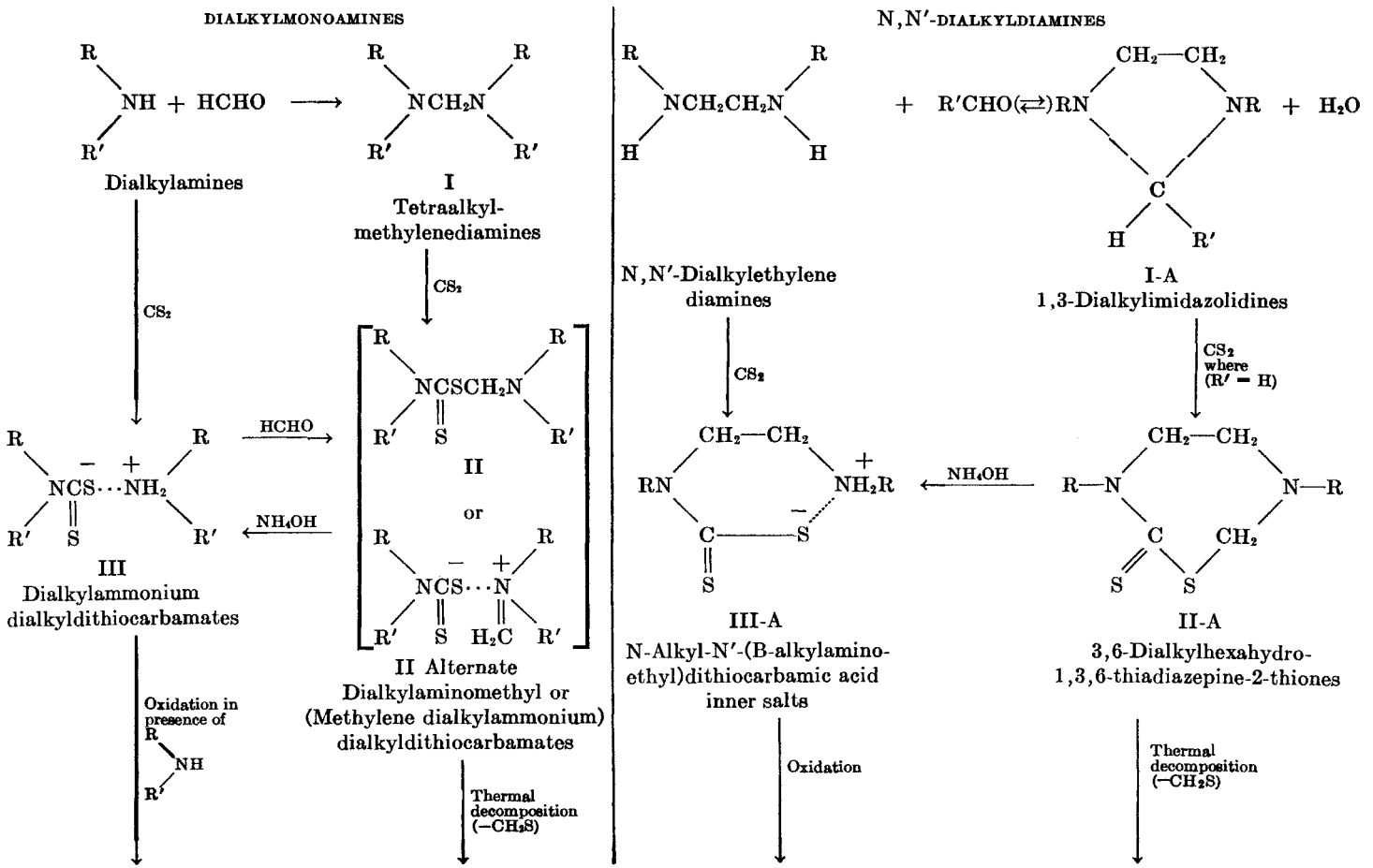
Thus, the similarity of II and the covalent sulfenamide conductivities supports the covalent ester structure, II, rather than the electrovalent structure, II-alternate, proposed by Levi. Further evidence for II rather than II-alternate is based on the high solubilities in benzene and ether and the low melting points exhibited by this type of compound, for in this respect they also resemble the covalent sulfenamide. However, the corresponding salts (III) from which they may be derived show, as would be predicted, low solubilities in these solvents and high melting points.

Fisher-Hirschfelder-Taylor models show that the suggested aminomethylene thioester structure is arranged in such a way that, for normal bond angles the sulfur and nitrogen atoms are forced close together,  perhaps close enough to interact and to produce a strain sufficiently large to explain the ease of splitting of the molecule by aqueous alkali (including ammonia), to produce

[2] These conductivities in nitrobenzene were determined by Mr. P. H. Biddison of this laboratory.

CHART I

SUMMARY OF AMINE-ALDEHYDE-CARBON DISULFIDE REACTIONS



R
NCSN
R'
S
V
Dialkylthiocarbamyl-sulfenamides
Thermal decomposition
R
NCN
R'
S
IV
Tetraalkylthioureas
CH2—CH2
RN
NR
C
S
V-A
2,5-Dialkyltetrahydro-1,2,5-thiadiazine-6-thiones
thermal decomposition
H2C—CH2
IV-A
1,3-Dialkyl-2-imidazolidinethiones

dithiocarbamate salts. This reaction was noted by Levi and was confirmed by us for both open chain and heterocyclic compounds.

Whereas the dialkylamine-formaldehyde condensation forms methylenediamines (I), reactions of N,N′-dialkylethylenediamines with aldehydes result in the formation of the heterocyclic imidazolidine ring (I-A). The preparation and properties of 1,3-diaryl- and 1,3-diaralkyl-imidazolidines have been studied

TABLE I

PROPERTIES OF 1,3-DIALKYLIMIDAZOLIDINES (I-A)

R IN IMIDAZOLIDINE FORMULA (I-A)	R′	YIELD,[a] %	DISTILLATION RANGE, °C./MM.	n_D^{25}	d_4^{25}	ANALYSES, N	
						Calc'd	Found[b]
Ethyl	H	65	65.5/35	—	0.858	21.86	21.60
Ethyl	Propyl	85.5	68–73/10	1.4473	.845	16.45	16.20
Ethyl	Phenyl	60.5	94/2.5	1.5128	.945	13.71	13.79
Allyl	H	64	73–74.5/10	1.4708	.887	18.40	18.20
Allyl	Propyl	80.5	96–97/10	1.4666	.868	14.40	14.43
Allyl	Phenyl	75	114/2.5	1.5265	.957	12.26	12.25
Isopropyl	H	73.5	67/10	1.4479	.851	17.92	18.10
Isopropyl	Propyl	81	91.5–93/10	1.4520	.856	14.12	14.03
Isopropyl	Phenyl	69	114/2.5	1.5111	.947	12.05	12.00
n-Butyl	H	81.5	105–106/10	1.4497	.846	15.19	15.20
n-Butyl	Propyl	87.5	121–125/10	1.4511	.842	12.37	12.15
n-Butyl	Phenyl	86	110–111/0.7	1.5001	.919	10.75	10.75
1-Methylbutyl	H	81	120.5/10	1.4570	.857	13.19	13.28
1-Methylbutyl	Propyl	85.5	103–107/2.5	1.4540	.849	11.01	11.10
1-Methylbutyl	Phenyl	90	116–118/0.7	1.4987	.916	9.68	9.71
Cyclohexyl	H	79	146/2.5	1.5049	.973	11.85	11.80
Cyclohexyl	Propyl	67.5	135–137/0.7	1.5005	.958	10.06	10.16
Cyclohexyl	Phenyl	67.5	m.p. 59.2–59.6 (corr.)	—	—	8.96	8.95
Phenyl	H	66	m.p. 124.6–124.8[c]	—	—	12.49	12.47
Phenyl	Propyl	37.5	m.p. 80.0–80.8 (corr.)	—	—	10.51	10.48
Phenyl	Phenyl	82.5	m.p. 136.4–136.8[d] (corr.)	—	—	9.32	9.25
2-Ethylhexyl	H	90.5	132/0.7	1.4588	.818	9.42	9.35
2-Ethylhexyl	Propyl	87	158–159/0.7	1.4594	.844	8.27	8.31
2-Ethylhexyl	Phenyl	81.5	164/0.7	1.4908	.893	7.51	7.60

[a] The yield was determined of purified compound calculated to 0.5% and based on diamine reactant. [b] The nitrogen analyses were carried out by the micro-Friedrich-Kjeldahl method. [c] Bischoff (10) reported 124°. [d] Moos (9) reported 137°.

by van Alphen (6) Lob (7), Rameau (8), Moos (9), Bischoff (10), and Scholtz and Jaroff (11). However, 1,3-dialkylimidazolidines have not been reported in the literature. Consequently, a compilation of properties of those prepared for this investigation is presented in Table I. Their synthesis was achieved by the condensation of each of three aldehydes: formaldehyde, butyraldehyde, and benzaldehyde with N,N′-disubstituted ethylenediamines in which the substitutents were ethyl, allyl, isopropyl, *n*-butyl, 1-methylbutyl, cyclohexyl, phenyl, and 2-ethylhexyl. This condensation proceeded most readily with formaldehyde,

with or without a solvent, giving a good yield of the corresponding 1,3-imidazolidine. With butyraldehyde and benzaldehyde, the reactions producing 2-substituted imidazolidines proceeded more slowly, and were aided by warming in the presence of toluene and separation of the water formed.

1,3-Dialkylimidazolidines and carbon disulfide reacted at room temperature in ether or alcohol. The product which precipitated on cooling the reaction mixture was a fairly pure, yellow crystalline material with no odor. Analyses for sulfur and nitrogen corresponded to a reaction between equimolar quantities of each reactant. An interpretation of the imidazolidine-carbon disulfide reaction is facilitated by considering an imidazolidine as a methylenediamine in which the nitrogen atoms are linked by an ethylene chain. Thus, the formation of a 3,6-dialkylhexahydro-1,3,6-thiadiazepine-2-thione (II-A) has been postulated as the diamine analog of II. Fisher-Hirschfelder-Taylor models of these compounds show that the ring atoms form a strain-free seven-membered ring. This model,

TABLE II

3,6-DIALKYLHEXAHYDRO-1,3,6-THIADIAZEPINE-2-THIONES (II-A)

R IN THIADIAZEPINE FORMULA (II-A)	REACTION SOLVENT	YIELD, %	M.P., °C. (CORR.)	ANALYSES			
				Calc'd		Found	
				N	S	N[a]	S[b]
Ethyl	ether	86	68.4–69.4	13.72	31.40	13.82	31.52
Isopropyl	alcohol	82	103.0	12.07	27.58	12.05	27.20
n-Butyl	ether	61	61.4–61.8	10.78	24.59	10.75	24.55
Cyclohexyl	alcohol	97	98 –99.4	8.97	20.51	8.94	20.20

[a] The nitrogen analyses were carried out by the micro-Friedrich-Kjeldahl method.
[b] The sulfur analyses were made with a semi-micro Parr bomb.

however, lacks the symmetry and stability of the five-membered imidazolidine rings which may explain in part the observed decomposition of the former to the latter. The properties of four thiadiazepines are presented in Table II. An attempt to react 1,3-diphenylimidazolidine with carbon disulfide gave no evidence of reaction.

A different type of reaction was noted when the 2-position of the imidazolidine ring contained an alkyl (propyl) or aryl (phenyl) substituent. The product which separated from the mixture was not a thiadiazepine derivative, but an N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acid inner salt (III-A). The latter was also the product of a dialkylethylenediamine-carbon disulfide reaction (Part I).

The failure to form the expected thiadiazepines from the 2-substituted imidazolidines may be related to the sluggishness with which these imidazolidines were formed. If the reaction of aldehyde with diamine to form imidazolidine and water is reversible, which is likely, it is indicated that the reverse reaction, or hydrolysis, took place much more readily with the 2-substituted imidazolidines. It would then be concluded that, in reacting the 2-substituted imidazolidines

with carbon disulfide in alcohol, hydrolysis first took place to form the original dialkylethylenediamines, which then reacted with the carbon disulfide to form the highly insoluble inner salts of the N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acids (III-A).

An imidazolidine-2-thione(IV-A) was identified as the thermal-decomposition product of a hexahydro-1,3,6-thiadiazepine-2-thione. Similar degradation to the 5-membered ring was shown in Part I to occur in the decomposition of the N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acids (III-A), and their oxidation products, the 2,5-dialkyltetrahydro-1,2,5-thiadiazine-6-thiones (V-A). The odor which the thiadiazepine compounds developed on standing indicated the instability of the compounds and suggests that the imidazolidine-2-thione was formed by loss of thioformaldehyde from the ring. The decomposition appears to be greatly accelerated by traces of impurity in the product. The parallel thermal decomposition of the dialkylaminomethyl dithiocarbamate esters (II or II-A) to form thioureas has not been reported. Preliminary experiments in this laboratory here yielded complex reaction mixtures which have not been investigated further.

Levi reported that his dialkylammonium dithiocarbamate-formaldehyde products (II-alternate) on treatment with heavy-metal salt solutions precipitated the metal dithiocarbamates. Likewise, he reported their oxidation to thiuram disulfides. These observations of Levi were confirmed, and in addition, dilute ammonia water or an aqueous solution of a volatile amine with II was shown to effect removal of the methylene group leaving the original dialkylammonium salt of the dialkyldithiocarbamic acid (III).

In the diamine series, the hexahydro-1,3,6-thiadiazepine-2-thiones dissolved almost completely in dilute aqueous ammonia. Following volatilization of ammonia on standing in an open dish for a few hours, white crystalline solids precipitated in the water. These products were identified as the inner salts of N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acids (III-A). This easy hydrolytic splitting of the thiadiazepine ring with elimination of formaldehyde and the formation of a six-membered ring with an electrovalent linkage is exactly analogous to the splitting of the aminomethylene dithiocarbamate esters by aqueous alkali or ammonia to form the dithiocarbamate salts.

In carrying out the oxidation of the aminomethylene dithiocarbamate esters (II or II-alternate) and also of the thiadiazepines (II-A), these compounds were invariably first dissolved in dilute aqueous alkali. Hence the solution undoubtedly did not contain the unchanged starting materials, but contained dithiocarbamate salts instead. It is, therefore, not surprising that subsequent oxidation of the aqueous solutions produced thiuram disulfides (I) in the first case, and the 2,5-dialkyl tetrahydro-1,2,5-thiadiazine-6-thiones (V-A) from the cyclic dithiocarbamate inner salt intermediates (III-A) in the second case.

EXPERIMENTAL

Preparation of N',N'-cyclopentamethyleneaminomethyl N,N-cyclopentamethylenedithiocarbamate (Dithioester II or Salt II-alternate) by three methods. Method 1 (1). The reaction

between 0.20 mole of methylene-*bis*-piperidine and 0.20 mole of carbon disulfide was performed in 200 cc. of alcohol at 5–10°. The white solid which separated was filtered and recrystallized from alcohol, m.p. 59.0–59.5° (corr.).

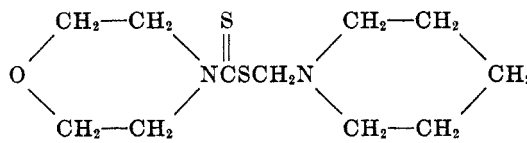
Method 2. (4). One-half mole of piperidinium N,N-cyclopentamethylenedithiocarbamate suspended in 200 cc. of alcohol was treated with 0.55 mole of formaldehyde (as 35–40% formalin). The slurry appeared partially to dissolve and after 12 hours at 0°, the white precipitate was filtered, m.p. 58.9–59.4°. Mixture m.p. with preparation of Method 1 was 58.8–59.4°, thereby establishing identity.

With each of these methods similar results were observed when the R and R′ groups were ethyl or oxadiethylene (from morpholine).

Method 3. Piperidinomethanol was prepared by slowly adding 0.5 mole of piperidine to 0.5 mole of formaldehyde (as 35–40% formalin). The temperature was kept below 15° by external cooling. This aqueous solution of piperidinomethanol was added slowly to a mixture of 0.32 mole (40 g.) of piperidinium N,N-cyclopentamethylenedithiocarbamate suspended in 250 cc. of alcohol. The slurry appeared to dissolve partially, but on cooling to 5°, it became pasty. The white product was recrystallized from alcohol, m.p. 58.6–59.2°; a mixture m.p. with the product from Method 1 was 58.8–59.4°.

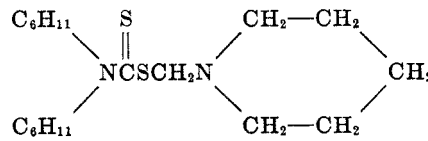
This reaction also was applied successfully to two other dithiocarbamates;

(*a*) An aqueous solution containing 0.1 mole of piperidinomethanol was added to a slurry of 0.067 mole (16.7 g.) of morpholinium N,N-oxadiethylenedithiocarbamate in 100 cc. of alcohol. After a few minutes the salt partially dissolved, insoluble matter was filtered, and the filtrate was placed in a refrigerator. After standing, crystalline plates were obtained, m.p. 88–90.5° (corr.), after recrystallization from ether-acetone. The product is assumed to have the structure:



Anal. Calc'd for $C_{11}H_{20}N_2OS_2$: N, 10.76; S, 24.62.
Found: N, 10.50; S, 24.75.

(*b*) An aqueous solution containing 0.1 mole of piperidinomethanol was added to 0.059 mole (25.7 g.) of dicyclohexylammonium dicyclohexyldithiocarbamate suspended in 75 cc. of alcohol. After a little agitation the slurry dissolved. The solution was poured into water whereupon a yellow oil separated. This oil crystallized on cooling. After washing with ether, the product melted at 114.5–116° (corr.). The structure is presumably:



Anal. Calc'd for $C_{19}H_{34}N_2S_2$: N, 7.90; S, 18.08.
Found: N, 7.42; S, 18.35.

Reaction of N′,N′-dialkylaminoethyl N,N-dialkyldithiocarbamates (II or II-alternate) with amines. A small quantity of each of the above dithioesters II (II-A) was suspended in water and sufficient amine (ammonia, ethylamine, etc.) added to dissolve the material. The solutions were allowed to stand in a watch glass exposed to air. White crystals precipitated during evaporation of the solvent. They were identified as the corresponding amine salt of the dithiocarbamic acid (III) by mixture melting point determinations with authentic samples.

Oxidation of II (or II-alternate) to thiuram disulfides. A dilute alkali solution of each of the above dithioesters II (or salt II-alternate) was oxidized with iodine-potassium iodide at

room temperature. The precipitated oxidation products were identified as thiuram disulfides by mixture melting point determinations with authentic samples.

Preparation of imidazolidines (I-A). In addition to the diamines described in Part I, several additional N,N′-dialkyl- and N,N′-diphenyl-ethylenediamines were used for the preparation of imidazolidines. They were prepared in the usual manner from the monoamine and ethylene dichloride. N,N′-diallylethylenediamine is a colorless liquid, b.p. 67.5–70°/6 N,N′-diphenylethylenediamine distilled at 178–182°/2 and solidified in the receiver on cooling.

1,3-Disubstituted imidazolidines were prepared by slowly adding formaldehyde (as 35–40% formalin) in 10% molar excess to the diamine. A highly exothermic reaction ensued and the addition of formalin was regulated to keep the temperature below 50°. When diethyl-, diisopropyl-, and dicyclohexyl-ethylenediamines were used, formation of the diamine hydrate on addition of formalin caused solidification of the reaction mixture; on further addition of formalin, the mass liquidified. At the completion of most of the reactions, two liquid phases—water and imidazolidine—were present. Separation of the diethyl-, diallyl-, and diisopropyl-imidazolidines was induced by salting.

The 2-propyl- and 2-phenyl-dialkylimidazolidines were prepared in warm toluene (50–60°) solution from the diamine and butyraldehyde, or benzaldehyde. The diamines which contained the larger N-substituents such as phenyl or 2-ethylhexyl reacted somewhat sluggishly and these reaction mixtures were refluxed for one hour. The by-product water from each reaction was withdrawn and the toluene removed by distillation.

The liquid imidazolidines were purified by distillation through a six-inch Vigreux column. Yields shown in Table I are those of purified products. Solid products were recrystallized from benzene.

Preparation of 3,6-dialkylhexahydro-1,3,6-thiadiazepine-2-thiones (II-A). Solutions of 1,3-diethyl-, diisopropyl-, dibutyl-, and dicyclohexyl-imidazolidines (20%) in the solvent indicated in Table II were treated with a 10% molar excess of carbon disulfide, added at a sufficiently slow rate to permit dissipation of the heat of reaction. The solutions became yellow and were maintained at room temperature for two hours; then they were placed in the refrigerator overnight. An oily layer separated from the diethyl- and dibutyl-imidazolidine reaction mixtures; on cooling in a Dry Ice-acetone bath, the oils solidified to canary yellow crystals. Diisopropyl- and dicyclohexyl-imidazolidine-carbon disulfide products separated as solids and were recrystallized from slightly warm acetone; the ease of thermal decomposition necessitated caution in purification.

Thermal decomposition of 3,6-dialkylhexahydro-1,3,6-thiadiazepine-2-thiones (II-A) to 1,3-dialkylimidazolidine-2-thiones (IV-A). A few grams of each thiadiazepine (II-A) (Table II), dissolved in alcohol, was refluxed. The white solid (trithioformaldehyde?) which precipitated was filtered. The imidazolidine-2-thiones (IV-A) were crystallized from the alcoholic solution and identified by a mixture melting point with an authentic sample in each case.

The 1,2,3-trisubstitutedimidazolidine-carbon disulfide reaction. A solution of 9.8 g. of 1,3-dicyclohexyl-2-phenylimidazolidine in 30 cc. of alcohol was agitated while 2.5 g. of carbon disulfide were added slowly. A white solid began to precipitate almost immediately; after two hours it was filtered and washed with acetone, yield 8.9 g. The product decomposed at 166°; it was identified as N-cyclohexyl-N-(β-cyclohexylaminoethyl)dithiocarbamic acid inner salt (III-A, R = cyclohexyl):

Anal. Calc'd for $C_{15}H_{28}N_2S_2$: N, 9.33; S, 21.3.
Found: N, 9.41; S, 21.2.

This reaction was applied to other imidazolidines as follows: the 1,3-diethyl-2-propyl-, 1,3-diisopropyl-2-propyl-, and 1,3-dicyclohexyl-2-propyl- imidazolidines also gave III-A as shown by the temperatures and manner of decomposition of the reaction products.

The 3,6-dialkylhexahydro-1,3,6-thiadiazepine-2-thione (II-A). *Reaction with ammonia.* A few grams of II-A (Table II) in dilute ammonia water was stirred to dissolve the compound and this was then filtered; usually a very small amount of insoluble matter was

present. The clear filtrate was placed in an evaporating dish for a few hours whereupon white crystals precipitated. They were identified as N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acids (III-A) by the temperature and nature of decomposition.

Oxidation of 3,6-dialkylhexahydro-1,3,6-thiadiazepine-2-thiones (II-A) to 2,5-dialkyltetrahydro-1,2,5-thiadiazine-6-thiones (V-A). A solution of 0.01 mole II-A (Table II) in 100 cc. of 0.1 *M* sodium hydroxide was stirred while aqueous iodine-potassium iodide solution was added dropwise. The oxidation product precipitated and after recrystallization was identified as the corresponding 2,5-dialkyltetrahydro-1,2,5-thiadiazine-6-thione (V-A) by mixture melting point determinations with authentic samples.

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SUMMARY

1. The reaction products of methylenediamines and carbon disulfide have been postulated as dithioesters, N′,N′-dialkylaminomethyl N,N-dialkyldithiocarbamates.

2. A series of new 1,3-dialkyl-, 1,3-dialkyl-2-propyl-, and 1,3-dialkyl-2-phenylimidazolidines was prepared.

3. The addition of carbon disulfide to 1,3-dialkylimidazolidines gave compounds to which have been assigned the structure of 3,6-dialkylhexahydro-1,3,6-thiadiazepine-2-thiones. Decomposition of the latter by loss of thioformaldehyde yielded 1,3-dialkylimidazolidine-2-thiones. With dilute ammonium hydroxide the thiadiazepines formed the inner salts of N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acids while halogens oxidized the aqueous solutions to 2,5-dialkyl-1,2,5-thiadiazine-6-thiones.

4. No reaction of 1,3-diphenylimidazolidine with carbon disulfide was evident.

5. If the 2-position on a 1,3-dialkylimidazolidine was substituted by an alkyl (propyl) or aryl (phenyl) group, the reaction with carbon disulfide formed the inner salt of an N-alkyl-N-(β-alkylaminoethyl)dithiocarbamic acid.

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