acetate. The ethyl acetate solution was dried over sodium sulfate and evaporated *in vacuo* to dryness. The residue was identified as *N*-(β-hydroxyethyl)benzylcarbamate (mixed melting point and infrared); yield 82%. Similar results were obtained with compounds 19,21,22 (Table I) and compounds 3,4,11 (Table II).

The qualitative 2,4-dinitrophenylhydrazine and the semicarbazide tests were performed by the standard procedure.[9] The infrared spectra were determined in chloroform solutions on a Perkin-Elmer Model 21 Spectrophotometer.

HAIFA, ISRAEL

(9) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 4th ed., Wiley, New York, 1956.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF DELAWARE]

Reactions of α,α-Dialkyl-α-mercaptoacetamides with Carbonyl Compounds

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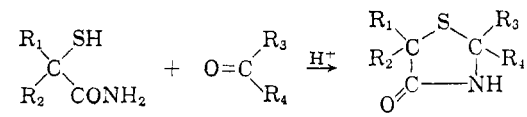
The condensation of α,α-dialkyl-α-mercaptoacetamides with aliphatic aldehydes gave a series of high-melting dimeric 4-thiazolidinones all having a characteristic infrared absorption in the region of 2.94 μ. In cases where the substituents at position 5, or 2, were different, two isomeric dimers were isolated which were then *N*-methylated to the same product. The same mercapto amides condensed with aromatic aldehydes or ketones to give monomeric 4-thiazolidinones having a characteristic infrared absorption in the region of 3.14 μ. Alkaline hydrolysis of both 5,5-diphenyl-2-imino-4-thiazolidinone and 5,5-diphenyl-2,4-thiazolidinedione yielded α,α-diphenylacetamide and gave none of the expected α,α-diphenyl-α-mercaptoacetamide. In general, the carbamyldiphenylmethylsulfur bond and the carboxydiphenylmethylsulfur bond were cleaved by bases with the loss of elemental sulfur.

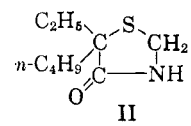
This study was prompted in part by the recent availability of α,α-dialkyl-α-mercaptoacetamides.[2] The objective of the present work was their use in the synthesis of derivatives of 4-thiazolidinones.

Previous investigators have explored a variety of condensation reactions of carbonyl compounds with β-mercaptoamines to form thiazolidines.[3,4] Although a few examples of reactions of thioglycollamide with carbonyl compounds have been reported, the literature contains no reference to the use of α,α-dialkyl-α-mercaptoacetamides. The reactions of thioglycollamide with benzaldehyde[5] and with *n*-heptaldehyde[6] gave the corresponding 2-substituted 4-thiazolidinones. Evidence given for the structure of 2-phenyl-4-thiazolidinone was the lack of reaction with sodium nitroprusside reagent and with cold sodium plumbite, and the fact that the infrared spectrum indicated the absence of the SH group and the presence of the NH group.[5]

In the present work we have found that the α,α-dialkyl-α-mercaptoacetamides react readily with a variety of carbonyl reagents in the presence of mineral acids, under both hydrous and anhydrous conditions, to give the corresponding di-, tri-, and tetrasubstituted 4-thiazolidinones. In cases where an aliphatic aldehyde was employed as the carbonyl



reagent, high melting 4-thiazolidinones were obtained. For example, the reaction of α-ethyl-α-mercapto-*n*-caproamide with formalin gave a mixture of isomers (IIa) and (IIb), both of which had an analysis corresponding to II. Structure



II

II indicates the presence of only one asymmetric carbon atom; thus, only one racemate should be expected. Inasmuch as two isomeric compounds, IIa and IIb, were actually isolated, the possibility of bimolecular compounds was investigated. Molecular weight determinations indicated dimeric values for each of the isomers. Bimolecular compounds composed of two units of II would have the two necessary asymmetric centers.

Numerous examples of hydrogen-bonded dimers of cyclic amides have been reported, both in solution[7-9] and in the crystalline state.[10,11] The occur-

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(3) S. Ratner and H. T. Clarke, *J. Am. Chem. Soc.*, **59**, 200 (1937).

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(7) S. Mizushima, T. Simanouti, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba, and O. Fujioka, *J. Chem. Soc.*, **72**, 3490 (1950).

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(9) M. Tsuboi, *Bull. Chem. Soc. Japan*, **22**, 215 (1949); *Chem. Abstr.*, **45**, 2778 (1951).

(10) D. G. O'Sullivan and P. W. Sadler, *J. Chem. Soc.*, 2202 (1956).

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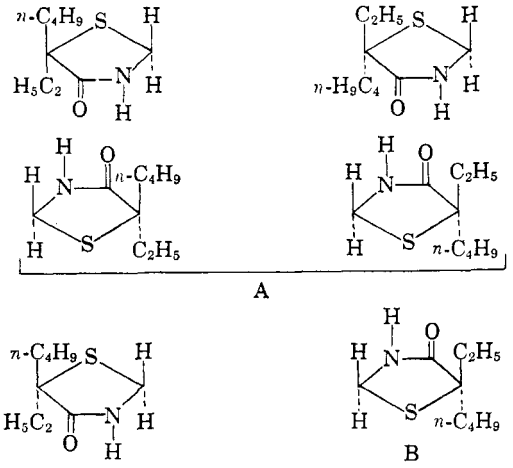
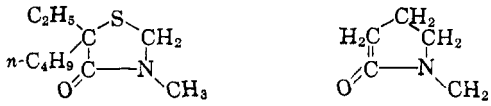
rence and separation of isomeric hydrogen-bonded dimers, however, have not been reported. Amides and cyclic amides are prone to form strong intermolecular bonds.[7,12] Cyclic amides are more apt to form ring dimers due to the geometrically rigid *cis-* arrangement of the amide. Dipolar forms of the resonance hybrid (sometimes called dipolar mesomers) undoubtedly contribute to the strong tendency of cyclic amides to dimerize. For example, δ-valerolactam has been shown to be highly dimerized even in very dilute solutions.[7,8] Fischer observed about 70% dimerization of 2-oxazolidinone in a 0.6% (by weight) solution of 2-oxazolidinone in benzene.[12] Apparently the upper limit for the molecular association factors of cyclic amides is 2.

In view of these facts it seems reasonable that the 5,5-dialkyl-4-thiazolidinones, which are cyclic amides, could have a hydrogen-bonded, ring-dimer structure. Such structures would account for the occurrence of two isomeric dimers when the substituents at position 5, or 2, were different. The dimeric structure is supported by the observed molecular weights Consideration of structures A and B further indicates that two dimeric forms, one a racemic modification (A) and the other *meso* (B), should be obtained. This was realized experimentally. Similar structures would account for the formation of two isomeric 4-thiazolidinone



dimers (Va, Vb) from the reaction of acetaldehyde with α-ethyl-α-mercapto-*n*-butyramide. In this case the substituents at position 5 were identical, but those at position 2 were different. For other cases of the formation of isomeric dimers, see Table I. If the substituents at position 5 are identical and the 4-thiazolidinone is unsubstituted at position 2, then only one form of the dimer should be produced. When both substituents were ethyl groups, only one compound (I), which was dimeric, was actually isolated in 84% yield.

The dimers were easily *N*-methylated to produce an abrupt change in physical properties, notably a marked lowering of melting points. For example, the methylation of the dimer (IIa), m.p. 181–182°, gave the same *N*-methyl derivative (IIc) as that obtained from the methylation of the isomeric dimer (IIb), m.p. 241–242°. The monomeric products (IIc) from both methylation reactions distilled at the same temperature, had the same index of refraction, and gave identical infrared spectra. The molecular weight and elementary analysis agreed with the monomeric formula ($C_{10}H_{19}NOS$) for 5-*n*-butyl-5-ethyl-3-methyl-4-thiazolidinone (IIc). The properties of the oil, which was quite mobile and distilled readily at 111° (0.34 mm.), are those that might be expected for IIc, whose infrared spectrum was very similar to that of the structurally similar compound, *N*-methyl-2-pyrrolidinone. Another example of a



marked lowering of melting point after methylation of associated molecules was noted by Hopkins and Hunter in their studies of the associating effect of the hydrogen atom.[13]

In contrast to the 5,5-dialkyl-4-thiazolidinones unsubstituted at position 2 described above, the 2,2,5-trisubstituted 4-thiazolidinones obtained from aromatic aldehydes and the 2,2,5,5-tetrasubstituted 4-thiazolidinones obtained from aliphatic and aromatic ketones exhibited little or no tendency to dimerize. Molecular weight determinations in the series of 4-thiazolidinones having an aromatic substituent or two aliphatic substituents at position 2 indicated values close to those calculated for the monomers. The effect of substituents at position 2 on properties of 4-thiazolidinones is clearly seen in Table I. In no case were two compounds isolated when the 4-thiazolidinone was disubstituted at position 2 or monosubstituted with an aromatic group at position 2. It is possible that dimer formation is inhibited due to steric bulk in those 4-thiazolidinones which are highly substituted at position 2 or those which have at least one bulky group at position 2.

Evidence that the condensation products of α,α-dialkyl-α-mercaptoacetamides and carbonyl compounds had a 4-thiazolidinone structure was given by the fact that none of the compounds listed in Table I reacted with sodium nitroprusside reagent. The infrared spectra indicated the absence of the SH group and the presence of the NH group. The infrared spectra also exhibited several prominent amide bands.[14]

The infrared spectra of the 4-thiazolidinone dimers. IIa and IIb, though not identical, exhibited

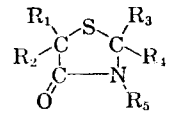
(12) Ernst Fischer, *J. Chem. Soc.*, 4525 (1952).

(13) G. Hopkins and L. Hunter, *J. Chem. Soc.*, 638 (1942).

(14) T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **29**, 611 (1958).

TABLE I

4-THIAZOLIDINONES

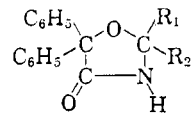


	R_1	R_2	R_3	R_4	R_5	Yield, %	M.P. or B.P.	Calcd. M.W.	Found M.W.[a]	Infrared Wave Length, μ N—H	C=O		Calcd. C	Calcd. H	Calcd. N	Found[b] C	Found[b] H	Found[b] N
I	C_2H_5	C_2H_5	H	H	H	84	265–267	159	310	2.95	6.02	I	52.79	8.23	8.80	53.07	8.16	8.75
IIa	C_2H_5	n-C_4H_9	H	H	H	89[c]	181–182	187	350	2.94	6.04	IIa	57.71	9.15	7.48	57.76	9.13	7.43
IIb	C_2H_5	n-C_4H_9	H	H	H		241–242	187	354	2.94	6.05	IIb	57.71	9.15	7.48	57.74	8.83	7.45
IIc	C_2H_5	n-C_4H_9	H	H	CH_3	83	111/0.34 mm.[d]	201	196	—	5.98	IIc	59.66	9.51	6.96	59.36	9.22	6.58
IIIa	C_2H_5	i-C_4H_9	H	H	H	80[c]	169–171	187	364	2.94	6.03	IIIa	57.71	9.15	7.48	58.21	9.24	7.32
IIIb	C_2H_5	i-C_4H_9	H	H	H		204–206	187	327	2.94	6.04	IIIb	57.71	9.15	7.48	57.90	9.07	7.64
VIa	C_2H_5	C_6H_5	H	H	H	24[c]	186–187	207	409	2.95	6.05	IVa	63.73	6.32	6.76	64.03	6.37	
IVb	C_2H_5	C_6H_5	H	H	H		244–245	207	415	2.95	6.05	IVb	63.73	6.32	6.76	63.54	6.39	6.69
IVc	C_2H_5	C_6H_5	H	H	CH_3	72	133/1.2 mm.[e]	221	210	—	6.00	IVc	65.12	6.83	6.33	64.62	6.74	5.81
Va	C_2H_5	C_2H_5	CH_3	H	H	72[c]	164–165	173	323	2.98	6.01	Va	55.45	8.73	8.08	55.55	8.67	8.06
Vb	C_2H_5	C_2H_5	CH_3	H	H		190–191	173	317	2.92	6.06	Vb	55.45	8.73	8.08	56.00	8.83	7.94
Vc	C_2H_5	C_2H_5	CH_3	H	CH_3	41	82–83/0.9 mm.[f]	187	194			Vc	57.71	9.15	7.48	57.57	9.15	7.37
VI	C_2H_5	C_2H_5	C_2H_5	H	H	40	139–140	187	353	2.97	6.04	VI	57.71	9.15	7.48	57.68	8.97	7.45
VII	C_2H_5	C_2H_5	C_6H_5	H	H	94	117–118	235	214	3.14	6.02	VII	66.34	7.28	5.95	66.18	7.34	5.93
VIII	C_2H_5	C_2H_5	p-$C_6H_4CH_3$	H	H	83	99–99.5	249	236	3.14	6.01	VIII	67.43	7.68	5.62	67.73	7.58	5.56
IX	C_2H_5	C_2H_5	p-$C_6H_3OCH_3$	H	H	78	155–156	265	272	3.15	5.98	IX	63.36	7.22	5.28	63.48	7.28	5.28
X	C_2H_5	C_2H_5	3,4-$C_6H_4(OCH_3)_2$	H	H	93	130–131	295		3.00 3.13	5.97	X	60.99	7.17	4.74	61.22	7.04	4.69
XI	C_2H_5	C_2H_5	p-$C_6H_4N(CH_3)_2$	H	H	69	146–146.5	278				XI	64.71	7.97	10.06	64.35	7.96	10.02
XII	C_2H_5	C_2H_5	CH_3	CH_3	H	98	117–117.5	187	205	3.13	5.93	XII	57.71	9.15	7.48			7.45
XIII	C_2H_5	C_2H_5	CH_3	CH_3	CH_3	64	81–82/0.8 mm.[g]	201	190	—	6.00	XIII	59.66	9.51	6.96	59.19	9.21	6.81
XIV	C_2H_5	C_2H_5	C_2H_5	CH_3	H	86	74	201	201	3.10	5.94	XIV	59.66	9.51	6.96	60.05	9.31	6.94
XV	C_2H_5	C_2H_5	$CH(CH_3)_2$	CH_3	H	88	133/0.45 mm.[h]	215	209	3.16	6.02	XV	61.35	9.83	6.50	61.58	9.71	6.41
XVI	C_2H_5	C_2H_5	C_2H_5	C_2H_5	H	80	132/0.35 mm.[i]	215	228	3.12	6.05	XVI	61.35	9.83	6.50	61.48	9.72	6.49
XVII	C_2H_5	C_2H_5	(Spirocyclopentyl)		H	85	117–118	213	212	3.14	6.01	XVII	61.93	8.98	6.57	62.46	8.98	6.54
XVIII	C_2H_5	C_2H_5	(Spirocyclohexyl)		H	51	123–124	227	212	3.17	5.98	XVIII	63.39	9.31	6.16	63.23	9.28	6.10
XIX	C_2H_5	C_2H_5	(Spirocycloheptyl)		H	74	135–136	241	275	3.16	6.00	XIX	64.68	9.60	5.80	64.93	9.63	5.76
XX	C_2H_5	C_2H_5	CH_3CO	CH_3	H	76	96–97	215		3.14	5.92	XX	55.78	7.96	6.51	56.20	7.88	6.49
XXI	C_2H_5	C_2H_5	$C_3H_6N_3O$[j]	CH_3	H	78	236–238 dec.	272				XXI	48.51	7.40	20.57	48.81	7.45	20.35
XXII	C_2H_5	C_2H_5	CH_3COCH_2	CH_3	H	46	75–76	229		3.15	5.95	XXII	57.61	8.35	6.11	57.52	8.15	6.09
XXIII	C_2H_5	C_2H_5	$C_9H_{16}NOS$[k]	CH_3	H	10	185–186	359	402	3.14	6.05	XXIII	56.94	8.43	7.81	57.20	8.32	7.76
XXIV	C_2H_5	n-C_4H_9	CH_3	CH_3	H	96	103–103.5	215	232	3.11	5.96	XXIV	61.35	9.83	6.50	61.60	9.64	6.48
XXV	C_2H_5	i-C_4H_9	CH_3	CH_3	H	96	100–101	215	251	3.10	5.94	XXV	61.35	9.83	6.50	61.67	9.56	6.47
XXVI	C_2H_5	C_2H_5	C_6H_5	CH_3	H	60	115–116	249	233	3.16	5.98	XXVI	67.43	7.68	5.62	68.13	7.68	5.58

[a] Rast method. [b] The authors are indebted to Merck Sharp and Dohme for these and subsequent analyses. [c] Before separation. [d] n_D^{25} 1.4924. [e] n_D^{25} 1.5714. [f] n_D^{25} 1.4954. [g] n_D^{25} 1.4881 [h] n_D^{25} 1.4978. [i] n_D^{25} 1.4968. [j] XXI is the semicarbazone of XX. [k] XXIII is the condensation product of XXII and α-ethyl-α-mercapto-n-butyramide.

TABLE II

4-OXAZOLIDINONES



	R_1	R_2	Yield, %	M.P., °	Calcd., M.W.	Found,[a] M.W.	Infrared Wave Length, μ N—H	Infrared Wave Length, μ C=O	Nitrogen, % Calcd.	Nitrogen, % Found
XLVI	H	H	70	248–249	239	482	2.96	6.03	5.86	5.81
XLVII	CH_3	H	24	218–219	253	434	2.99	6.02	5.53	5.76
XLVIII	CH_3	CH_3	93	242–243	267	281	3.14	5.87	5.24	5.21

[a] Rast method.

striking similarities. A characteristic, single, sharp infrared absorption band of strong intensity in the region of 2.94 μ, not present in the spectra of the 2-aryl or the 2,2-disubstituted 4-thiazolidinones, was observed for each of the dimeric 4-thiazolidinones in the crystalline state. On the other hand, each of the monomeric 4-thiazolidinones exhibited an N—H band in the region of 3.14 μ (Table I). These results are partially in agreement and partially at variance with the N—H bands reported for hydrogen-bonded dimers.[7,9,10,15,18]

The possibility of covalently bonded dimeric structures was considered, but no such structures could be written which would account for all the observed properties of the dimeric 4-thiazolidinones. A compound, bis-2,2′-(5,5-diethyl-2-methyl-4-thiazolidinonyl)methane (XXIII), containing two thiazolidinone rings covalently bonded through a methylene group was prepared. The molecular weight and infrared spectrum of XXIII, however, agreed with the pattern observed in the series of monomeric 4-thiazolidinones.

Benzilamide, the oxygen analog of diphenylmercaptoacetamide, was condensed with formaldehyde, acetaldehyde, and acetone to give three new 4-oxazolidinones (Table II). These compounds had properties and spectra similar to the 4-thiazolidinones substituted in the same positions.

The attempt to prepare α,α-diphenyl-α-mercaptoacetamide by the general procedure of Skinner, Elmslie, and Gabbert[2] for the preparation of α,α-disubstituted α-mercaptoacetamides was unsuccessful. The alkaline hydrolysis of 5,5-diphenyl-2-imino-4-thiazolidinone gave a mixture of diphenylacetamide and diphenylacetic acid. A shorter alkaline hydrolysis of 5,5-diphenyl-2,4-thiazolidinedione gave only diphenylacetamide and unchanged starting material. Both reactions resulted in the fission of the carbon-sulfur bond between positions 1 and 5.

The fact that the carboxydiphenylmethyl-sulfur bond and other related structures tend to undergo a similar fission quite readily was demonstrated by a number of reactions in alkaline media. For example, the ammonolysis of the methyl ester of diphenylmercaptoacetic acid at 0° gave a nearly quantitative yield of methyldiphenylacetate and elemental sulfur plus a small amount of diphenylacetamide. When diphenylmercaptoacetic acid was refluxed in 1.25*N* sodium hydroxide solution, a mixture of diphenylacetic acid, *p*-(phenylcarboxymethyl)triphenylacetic acid and elemental sulfur was obtained.

EXPERIMENTAL

5,5-Disubstituted 2-imino-4-thiazolidinones. These compounds were prepared by adding the corresponding α-bromodialkylacetyl bromide to a slurry of thiourea and dioxane at 92–94°. A marked improvement in the yields was effected by the use of this procedure, illustrated by the preparation of 5-*n*-butyl-5-ethyl-2-imino-4-thiazolidinone, the yield of which was raised from 53% to 83%. To a stirred mixture of 182 g. (2.4 moles) of thiourea and 600 ml. of dioxane at 92–94° was added dropwise, in 2 hr., 229 g. (0.8 mole) of α-bromo-α-ethyl-*n*-caproyl bromide. The reaction mixture was heated an additional 8 hr. with stirring at 92–94°. The yield was 132.5 g., m.p. 206–208°.

5,5-Disubstituted 4-thiazolidinone dimers. In a typical experiment 27 ml. (0.32 mole) of concd. hydrochloric acid was added, all at once, to a rapidly stirred heterogeneous mixture of 28 g. (0.16 mole) of α-ethyl-α-mercapto-*n*-capramide and 24.6 ml. (0.32 mole) of formalin. Within 2 seconds the mixture became homogeneous. Remaining homogeneous for a second, it then turned cloudy and changed to a thick paste while the temperature spontaneously rose to 70°. The precipitate solidified about 3 min. later, and the solid was found to a powder in the reaction mixture. Filtration left a residue which was triturated in 5% sodium hydroxide solution to remove the unchanged mercapto amide. The residue was washed with water and dried to give 26.7 g. of a mixture of 5-*n*-butyl-5-ethyl-4-thiazolidinone dimers (IIa, IIb), m.p. 180–215°. A separation of the mixture of dimers was accomplished by extraction of the more soluble and lower melting component (IIa) from the less soluble and higher melting component (IIb) as follows. The dried 26.7-g. mixture was ground to a paste in a small amount of methanol, diluted with 350 ml. of methanol, and heated to boiling. After cooling to room temperature and allowing the solid to settle, the mixture was separated by decantation

(15) W. Klemperer, M. W. Cronyn, A. H. Maki, and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 5846 (1954).

(16) S. E. Darmon and G. B. B. M. Sutherland, *Nature*, **164**, 440 (1949).

(17) R. A. Russell and H. W. Thompson, *Spectrochim. Acta*, **8**, 138 (1956).

(18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1958, pp. 208, 209.

and filtration of the remaining slurry. The residue was then extracted with two additional portions of methanol. The residue was treated with 350 ml. of boiling benzene and separated as above to yield, after drying, 12.4 g. of a white solid, m.p. 235–241°. Recrystallization from hot 80% aqueous acetic acid yielded 11.5 g. (0.061 mole) of IIb. Concentration of the methanol and benzene filtrates yielded crops of crystals which were separated by filtration and washed with very small portions of methanol. Successive crops were thus obtained. Recrystallization of the combined crops of crystals from methanol furnished 9.7 g. (0.052 mole) of IIa.

2,5,5-Trisubstituted-4-thiazolidinone dimers (from aliphatic aldehydes). These compounds were prepared by the condensation of the corresponding dialkylmercaptoacetamide and an aliphatic aldehyde with dry hydrogen chloride as the catalyst. To illustrate, dry hydrogen chloride was bubbled through a solution of 2.94 g. (0.02 mole) of α-ethyl-α-mercapto-*n*-butyramide in 4.4 g. (0.10 mole) of acetaldehyde at 10–20°. After 10 min. the reaction mixture partially solidified and remained perfectly white. Trituration of the mixture in 50 ml. of water and decantation of the supernatant liquid yielded a white solid which was separated from the mixture by filtration and washed with more water. After drying, treatment of the solid (2.5 g.) with 15 ml. of methanol left a 0.5 g. of residue, m.p. 184–187°, which was recrystallized several times from aqueous methanol to give 0.1 g. of 5,5-diethyl-2-methyl-4-thiazolidinone dimer (Vb). To the original methanol mother liquor (15 ml.) was added 8 ml. of water which precipitated 1.2 g. of a mixture of the components. The mother liquor from the 1.2 g. residue yielded three additional intermediate crops after the successive addition of three small portions of water. From the last filtrate a 0.15-g. solid fraction was obtained by adding about 40 ml. of water. After three recrystallizations from aqueous methanol, the 0.15-g. fraction gave 62 mg. of 5,5-diethyl-2-methyl-4-thiazolidinone dimer (Va). A fourth recrystallization failed to change the melting point.

2,5,5-Trisubstituted-4-thiazolidinones (from aromatic aldehydes). In a typical experiment a mixture of 5.9 g. (0.04 mole) of α-methyl-α-mercapto-*n*-butyramide and 5.3 g. (0.05 mole) of benzaldehyde, to which 4.15 ml. (0.05 mole) of concd. hydrochloric acid was added, warmed spontaneously to 60°. After remaining homogeneous for 1.5 hr. at 40–45°, the mixture gave a negative test for the mercapto group. Dilution with 50 ml. of water precipitated a viscous oil which soon solidified. Filtration of the mixture yielded a white solid which was washed with several portions of water and dried to give 8.8 g. of crude 5,5-diethyl-2-phenyl-4-thiazolidinone. Recrystallization from aqueous methanol in the first crop 6.3 g., m.p. 115–117°. A second recrystallization afforded the pure 4-thiazolidinone (VII).

2,2,5,5-Tetrasubstituted-4-thiazolidinones. In a typical experiment a solution of 7.0 g. (0.04 mole) of α-ethyl-α-mercapto-*n*-caproamide, 9.3 g. (0.16 mole) of acetone and 3.4 ml. (0.04 mole) of concd. hydrochloric acid was allowed to stand for 45 min. at 45–50°. At the end of this time the whole reaction mixture appeared to have solidified. Dilution of the mixture with 60 ml. of water gave a fluffy white precipitate which was filtered. The solid was triturated in 10% sodium hydroxide solution. After washing the residue with water and drying, 8.3 g. of 5-*n*-butyl-5-ethyl-2,2-dimethyl-4-thiazolidinone, m.p. 103–103.5°, were obtained. Recrystallization from acetone gave an analytical sample (XXIV).

N-Methyl derivatives of 4-thiazolidinones were prepared according to the procedure of Loudon and Ogg[19] for *N*-methylation of amides.

4-Oxazolidinones. The three 4-oxazolidinones listed in Table II were prepared by procedures similar to preparations of the 4-thiazolidinones substituted in the same positions.

(19) J. D. Loudon and J. Ogg, *J. Chem. Soc.*, 739 (1955).

Alkaline hydrolysis of 5,5-diphenyl-2-imino-4-thiazolidinone. A mixture of 20 g. (0.075 mole) of 5,5-diphenyl-2-imino-4-thiazolidinone and 150 ml. of 1.25*N* sodium hydroxide solution was refluxed for 18 hr. Filtration of the cooled reaction mixture yielded a 1.2-g. residue which was crystallized from aqueous ethanol and recrystallized to give 0.8 g. of diphenylacetamide. Acidification of the alkaline filtrate gave a dark brown oil which was dissolved in ether and extracted with saturated sodium bicarbonate solution. Evaporation of the extracted ether solution yielded approximately 4 g. of an intractable tar. Acidification of the bicarbonate solution yielded 10.4 g. of diphenylacetic acid.

5,5-Diphenyl-2,4-thiazolidinedione. A mixture of 8 g. (0.03 mole) of 5,5-diphenyl-2-imino-4-thiazolidinone and 100 ml. of 30% sulfuric acid was refluxed for 7.5 hr. While the mixture was refluxing, the solid changed completely to an oil and then to a solid again. The solid was separated by filtration, washed with water, and dried. Ether dissolved most of the solid and left 0.5 g. of insoluble residue. Evaporation of the ether furnished 7.2 g. of a white solid, m.p. 149–151°. Recrystallization from aqueous ethanol, it melted at 151–152°.

Anal. Calcd. for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N, 5.20. Found: C, 66.97; H, 4.19; N, 5.19.

Alkaline hydrolysis of 5,5-diphenyl-2,4-thiazolidinedione. A solution of 5.4 g. (0.02 mole) of 5,5-diphenyl-2,4-thiazolidinedione in 80 g. of a 2% sodium hydroxide solution (0.04 mole) was refluxed for 4 hr. After 3.75 hr. of refluxing, the homogeneous yellow solution turned opaque, and 15 min. later small droplets of a blue oil began to form at which point refluxing was stopped. After standing overnight at room temperature, the reaction mixture contained a white crystalline solid which was filtered and washed with water to furnish 1.3 g. of diphenylacetamide, m.p. 166–168°, identical with authentic sample. No other product could be isolated from the acidified filtrate except 3.3 g. of unchanged starting material.

Ammonolysis of the methyl ester of diphenylmercaptoacetic acid. A solution of 19.1 g. (0.074 mole) of the ester dissolved in 60 ml. of anhydrous methanol in a pressure bottle was saturated with anhydrous ammonia at −10° in 4 hr. The bottle was capped and refrigerated at 3–4° for 6 days. The methanolic solution was decanted from a yellow solid residue (13.2 g.). Evaporation of the methanol left a solid residue (4.0 g.). Treatment of the 13.2-g. residue with methanol dissolved most of it and left 2.2 g. of elemental sulfur. Fractional crystallization of the methanol soluble material gave 13.8 g. of methyl diphenylacetate and 0.4 g. of diphenylacetamide. No diphenylmercaptoacetamide could be isolated.

Action of sodium hydroxide on diphenylmercaptoacetic acid. A solution of 2.44 g. (0.01 mole) of diphenylmercaptoacetic acid in 16 ml. (0.02 mole) of 1.25*N* sodium hydroxide solution was refluxed for 10 hr. Filtration of the cooled hydrolyzate gave 0.4 g. of an unidentified solid, m.p. 151–152°. Acidification of the filtrate gave 1.5 g. of a solid which was soluble in saturated sodium bicarbonate solution. The acidic filtrate contained colloidal sulfur which precipitated from the solution after standing at room temperature. The bicarbonate soluble solid gave a negative test for the mercapto group with sodium nitroprusside reagent. Fractional crystallizations of the bicarbonate soluble solid from methanol and aqueous methanol gave 0.5 g. of diphenylacetic acid and 0.1 g. of *p*-(phenylcarboxymethyl)triphenylacetic acid.[20] Both were identified by mixed melting with the authentic compounds.

NEWARK, DEL.

(20) B. Witten and F. Y. Wiselogle, *J. Org. Chem.*, 6, 584 (1941).