

*Anal.* Calcd. for  $C_8H_4Cl_3NOS_2$ : S, 26.65. Found: S, 26.59.

A mixed melting point determination with a sample of trichloromethyl N-methylcarbamoyl disulfide (IIb) prepared from ethyl N-methylthionocarbamate showed no depression.

**Preparation of (Dithio)-formimidates.** A. Ethyl N-ethyl-1-(trichloromethylthio)-formimide.—A solution of 51.8 g. (0.279 mole) of trichloromethanesulfonyl chloride in 200 ml. of benzene was added dropwise during a period of 50 minutes to a stirred and cooled solution of 37.16 g. (0.279 mole) of ethyl N-ethylthionocarbamate and 22.1 g. (0.279 mole) of pyridine in 200 ml. of benzene. The reaction mixture was stirred for an additional 10 minutes and filtered. The residue was rinsed on the filter with a little benzene. The combined filtrate and rinsings were evaporated *in vacuo* to remove the benzene, and the residue was distilled through a small modified Claisen still. There was obtained 60.85 g. (77%) of crude ethyl N-ethyl-1-(trichloromethylthio)-formimide distilling at 88° (0.55 mm.) to 91° (1.0 mm.),  $n_D^{25}$  1.5362–1.5423. Upon redistillation through a small spinning band still fitted with a platinum band, there was obtained a fraction boiling at 87° (0.65 mm.) to 91° (0.70 mm.),  $n_D^{25}$  1.5372–1.5387, infrared max. at 1656  $cm^{-1}$  C=N (0.1% in chloroform).

*Anal.* Calcd. for  $C_8H_{10}Cl_3NOS_2$ : C, 25.50; H, 3.57; S, 22.69. Found: C, 25.97; H, 3.72; S, 22.82.

B. Ethyl N-Methyl-1-(trichloromethylthio)-formimide was prepared in a similar manner in 68% yield by the reaction of trichloromethanesulfonyl chloride with a mixture of ethyl N-methylthionocarbamate and pyridine in benzene: b.p. 79° (0.55 mm.) to 89° (1.0 mm.),  $n_D^{25}$  1.5490–1.5499.

*Anal.* Calcd. for  $C_8H_8Cl_3NOS_2$ : C, 22.36; H, 3.00; S, 23.87. Found: C, 23.23; H, 3.31; S, 25.87.

C. Ethyl N-Ethyl-1-(ethylthio)-formimide was prepared as described above in 92% yield by the addition of 29.1 g. (0.301 mole) of ethanesulfonyl chloride in 75 ml. of benzene to a solution of 40 g. (0.300 mole) of ethyl N-ethylthionocarbamate and 23.8 g. (0.301 mole) of pyridine in 200 ml. of benzene; b.p. 46° (0.05 mm.),  $n_D^{25}$  1.5064, infrared max. at 1642  $cm^{-1}$  C=N (0.1% in chloroform).

*Anal.* Calcd. for  $C_7H_{15}NOS_2$ : C, 43.49; H, 7.80; N, 7.25; S, 33.17. Found: C, 43.73; H, 7.94; N, 7.14; S, 33.45.

D. Ethyl N-*p*-Chlorophenyl-1-(*p*-chlorophenyldithio)-formimide.—A solution of 22.7 g. (0.127 mole) of *p*-chlorobenzenesulfonyl chloride in 100 ml. of benzene was added during 20 minutes to a stirred and cooled solution of 27.32 g. (0.127 mole) of ethyl N-*p*-chlorophenylthionocarbamate and 10.0 g. (0.126 mole) of pyridine in 200 ml. of benzene. After being stirred for an additional 10 minutes, the mixture was filtered and the filtrate evaporated *in vacuo*. The resulting residue crystallized when cooled to  $-76^\circ$ ; wt, 42.4 g. (94%), m.p. 30.5–35.5°. After two recrystallizations from pentane at  $-76^\circ$ , ethyl N-*p*-chlorophenyl-1-(*p*-chlorophenyldithio)-formimide was obtained as colorless flat needles melting at 33.5–35°, infrared maximum at 1639  $cm^{-1}$  C=N (0.1% in chloroform).

*Anal.* Calcd. for  $C_{15}H_{13}Cl_2NOS_2$ : C, 50.28; H, 3.66; S, 17.90. Found: C, 50.59; H, 3.86; S, 18.22.

**Action of Anhydrous Hydrogen Chloride on (Dithio)-formimidates.** A. Methyl N-Methyl-1-(trichloromethylthio)-formimide.—Anhydrous hydrogen chloride was bubbled for a few minutes through a solution of 2.0 g. (0.0074 mole) of ethyl N-methyl-1-(trichloromethylthio)-formimide in 50 ml. of benzene. The mixture was poured into a dish and allowed to evaporate to dryness. There remained 1.68 g. (94%) of crude trichloromethyl N-methylcarbamoyl disulfide (IIb) melting at 74–79°. Several recrystallizations from hexane raised the melting point to 82–82.5°. Mixed melting point determinations with samples of this compound prepared in the two previously described procedures showed no depression.

B. Ethyl N-*p*-Chlorophenyl-1-(*p*-chlorophenyldithio)-formimide.—Anhydrous hydrogen chloride was bubbled through a solution of 1.0 g. of ethyl N-*p*-chlorophenyl-1-(*p*-chlorophenyldithio)-formimide dissolved in 25 ml. of pentane. An oil began to separate immediately which soon solidified. After being allowed to stand for 0.5 hour, the mixture was filtered, and there was obtained 0.80 g. (87%) of crude product. This was recrystallized by dissolving it in 6 ml. of chloroform, filtering, and adding 14 ml. of pentane slowly. There was obtained 0.55 g. of *p*-chlorophenyl N-*p*-chlorophenylcarbamoyl disulfide as white needles. The infrared spectrum substantiated its identity with the product obtained directly from *p*-chlorobenzenesulfonyl chloride and ethyl N-*p*-chlorophenylthionocarbamate.

*Anal.* Calcd. for  $C_{13}H_9Cl_2NOS_2$ : S, 19.42. Found: S, 19.41.

WILMINGTON 98, DEL.

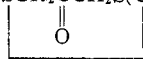
[CONTRIBUTION NO. 517 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

## The Chemistry of Some 5-*m*-Dithianones and Dithiacycloalkanones

BY E. G. HOWARD AND R. V. LINDSEY, JR.

RECEIVED JUNE 10, 1959

Dithiacycloalkanones,  $SCH_2CCH_2S(CH_2)_n$  where  $n = 2, 3$  and 4, have been prepared by the reaction of *sym*-dichloroac-



tone with the sodium salt of the appropriate dithiol. The cyclic thioketal, 5-*m*-dithianone (Va), was prepared by saponification and decarboxylation of 4-ethoxycarbonyl-5-*m*-dithianone after first inactivating the ketone group by conversion to a cyclic ketal by reaction with ethylene glycol. Numerous chemical transformations of these cyclic ketones are reported. Some new chemistry of 4-ethoxycarbonyl-5-*m*-dithianone including the separation of keto and enol forms also is described.

The only example of a cyclic ketone containing two ring sulfur atoms is 4-ethoxycarbonyl-5-*m*-dithianone (IIa), reported by Challenger and Miller.<sup>1</sup> These authors reported that hydrolysis of IIa resulted in cleavage of the ring. In an investigation of this reaction as a means for preparing the parent ketone, 5-*m*-dithianone (Va), we have found that the ethoxycarbonyl group can be

removed by hydrolysis and decarboxylation if the ketone group is first protected by conversion to a ketal.<sup>1a</sup>

4-Ethoxycarbonyl-5-*m*-dithianone<sup>1</sup> (IIa) was converted to the cyclic ketal IIIa by reaction with

(1a) Since this manuscript was submitted, A. Lüttringhaus and H. Prinzbach, *Ann.*, **624**, 79 (1959), have reported the direct hydrolysis of IIa to Va in sulfuric acid, as well as the synthesis of several derivatives of IIa also described in this paper.

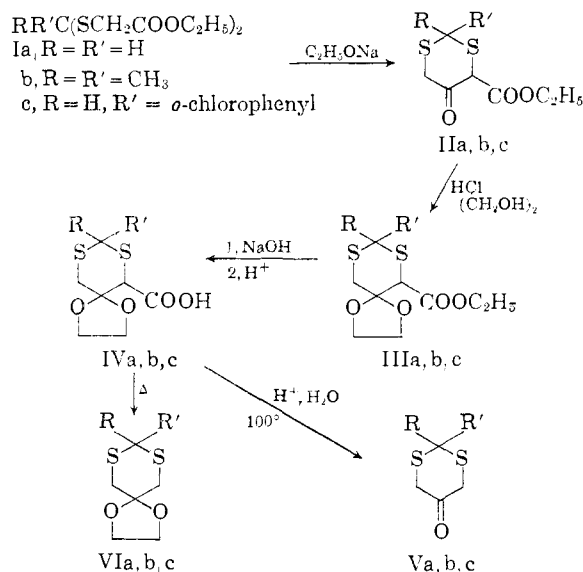
(1) F. Challenger and S. A. Miller, *This Journal*, 367 (1939).

TABLE I: REACTION PRODUCTS OF 5-*m*-DITHIANONES AND DITHIACYCLOALKANONES WITH AROMATIC ALDEHYDES

Type A		Type B		Empirical formula		Absorption maxima		Carbon, %		Hydrogen, %		Sulfur, %		Nitrogen, %	
Type	R	R'	M.p., °C.	Solvent	$\lambda$ , m $\mu$ ( $\epsilon$ )	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
A	CH <sub>3</sub>	CaH <sub>5</sub>	147-148.5	C <sub>6</sub> H <sub>5</sub> OH	264 (18,900), 387 (12,400)	68.05	69.82	4.55	4.70	20.66	20.81	7.07	7.00		
A	CH <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	252-255	C <sub>6</sub> H <sub>5</sub> OH	259 (11,100), 327 (15,700), 438 (24,400)	68.05	69.82	4.55	4.70	16.17	16.29	7.07	7.00		
A	CH <sub>3</sub>	$\alpha$ -C <sub>6</sub> H <sub>7</sub>	153.5-155	CHCl <sub>3</sub>	385 (11,500) <sup>a</sup>	76.09	75.82	4.42	4.34						
A	CH <sub>3</sub>	$\alpha$ -C <sub>6</sub> H <sub>5</sub> O	149-150.5	CHCl <sub>3</sub>	440 (16,500) <sup>a</sup>	57.94	57.83	3.47	3.56						
A	CH <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	234-235	CHCl <sub>3</sub>	400 (12,100) <sup>a</sup>	57.01	57.27	3.19	3.21						
A	CH <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> N(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>2</sub>	206-207	HCON(CH <sub>3</sub> ) <sub>2</sub>	320 (21,500), 432 (30,400) <sup>a</sup>	65.20	65.03	5.10	5.17			15.21	14.87		
A	C(CH <sub>3</sub> ) <sub>2</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> N(CH <sub>2</sub> ) <sub>2</sub>	225-227	CHCl <sub>3</sub>	330 (19,500), 433 (32,260) <sup>a</sup>	67.90	68.26	6.65	6.62						
B	CH <sub>3</sub>	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	70-71	C <sub>6</sub> H <sub>5</sub> OH	273 (10,900), 386 (13,500)	57.12	57.29	4.79	4.95	21.78	21.98	4.16	4.06		
B	CH <sub>3</sub>	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	132-133	C <sub>6</sub> H <sub>5</sub> OH	428 (25,300) <sup>a</sup>	46.30	46.45	3.34	3.51						
B	CH <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	115.8-117	CHCl <sub>3</sub>	390 (16,800) <sup>a</sup>	57.83	58.30	5.10	5.10			10.12	10.19		
B	CH <sub>3</sub>	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	159-160.5	CHCl <sub>3</sub>	428 (25,300) <sup>a</sup>	46.30	46.45	3.34	3.51						
B	CH <sub>3</sub>	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	133-134.5	CHCl <sub>3</sub>	393 (16,400) <sup>a</sup>	59.49	59.78	5.83	5.97						
B	CH <sub>3</sub>	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	152-153	CHCl <sub>3</sub>	465 (41,000) <sup>a</sup>	58.99	59.35	4.96	5.00						
B	CH <sub>3</sub>	CH=CH- <i>p</i> -C <sub>6</sub> H <sub>4</sub> N(CH <sub>2</sub> ) <sub>2</sub>	155-157	CHCl <sub>3</sub>	439 (30,000) <sup>a</sup>	58.99	59.35	4.96	5.00						
B	CH <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> N(CH <sub>2</sub> ) <sub>2</sub>	118-119	C <sub>6</sub> H <sub>5</sub> OH	300 (22,400), 365 (7800) <sup>a</sup>	19.76	19.41			19.76	19.41	5.01	5.04		
A	CH <sub>2</sub> CH <sub>2</sub>	H	129.5-130.5	C <sub>6</sub> H <sub>5</sub> OH	259 (9200), 414 (27,900)	22.97	23.05			22.97	23.05				

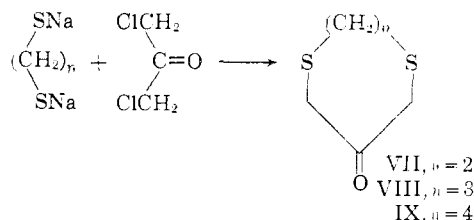
<sup>a</sup> Visible portion of spectrum only.

ethylene glycol. Saponification of the ester gave the acid IVa, which was readily converted to the corresponding acid chloride and amide. When the acid was heated at about 150°, decarboxylation to the ketal VIa occurred. 5-*m*-Dithianone (Va) was obtained directly from IVa when the latter was boiled in dilute acid. Yields in all of these steps were high. In fact, the ketone Va was obtained from IIa in an over-all yield of 83% without isolating IVa.



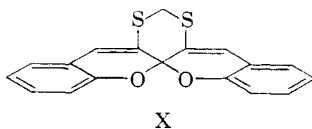
This synthesis also has been employed to obtain 2,2-dimethyl-(Vb) and 2-(*o*-chlorophenyl)-5-*m*-dithianone (Vc) from diethyl 4,4-dimethyl-3,5-dithiapimelate (Ib) and diethyl 4-(*o*-chlorophenyl)-3,5-dithiapimelate (Ic), respectively.

In addition, we have found a direct synthesis for cyclic ketones containing more than one methylene group between the sulfur atoms. Thus, compounds VII, VIII and IX were prepared by reaction of *sym*-dichloroacetone with the sodium salt of the appropriate  $\alpha,\omega$ -dithiol. Thus, 1,4-dithiacyclo-

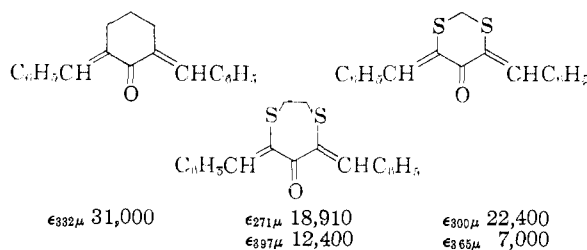


heptan-6-one (VII), 1,5-dithiacyclooctan-3-one (VIII) and 1,5-dithiacyclononan-3-one were obtained in yields of 70, 32 and 2.5%, respectively. An attempt to synthesize a 10-membered ring by this route gave only polymeric products.

The cyclic ketones reacted with aromatic aldehydes under the influence of mild bases such as piperidine to give bis-arylidene derivatives (Table I). These arylidene compounds are colored solids of moderate tinctorial strength. Only the mono-arylidene derivative was obtained from *p*-dimethylaminobenzaldehyde and VII. An unusual product, believed to be X, was obtained from



salicylaldehyde and Va. This structure is supported by elemental analyses and by the lack of carbonyl absorption in the infrared spectrum. The absorption spectra of the bis-arylidene derivatives have an absorption peak near the visible portion of the spectrum which is not shown by the corresponding cyclohexanone derivative.<sup>2</sup> Changing the size



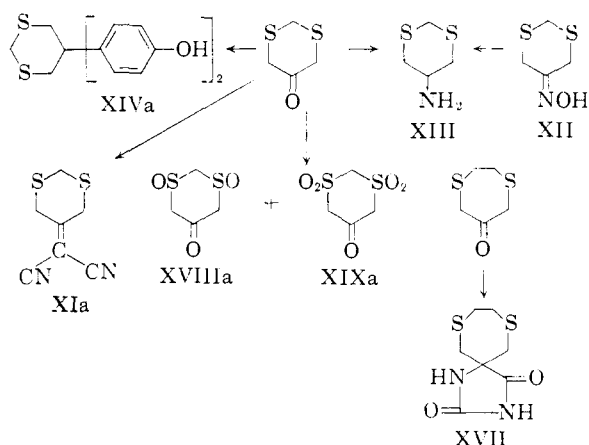
of the ring affects the intensity and spacing of the absorption maxima as shown by comparison of the data for the dibenzylidene derivatives of Va and VII. The spectra of derivatives prepared from *p*-dimethylaminobenzaldehyde had three peaks instead of two. These peaks were considerably shifted toward the visible, and showed an increase in the maximum.

A number of reactions of the cyclic ketones involving the keto group were examined. Condensation of Va and of VII with malononitrile without catalyst gave quantitative yields of the dicyanomethylene derivatives (XIa, d). An oxime (XIII), prepared from Va, was reduced with lithium aluminum hydride to the amine XIII. In the presence of concentrated hydrochloric acid, both Va and VII condensed with phenol to give the corresponding bis-*p*-hydroxyphenyl derivatives XIVa, d. A cyclic ketal (XV) and mercaptol (XVI) of VII formed readily with ethylene glycol and ethanedithiol, respectively, in the presence of anhydrous hydrogen chloride. Reaction of VII with ammonium carbonate and sodium cyanide gave the hydantoin XVII.

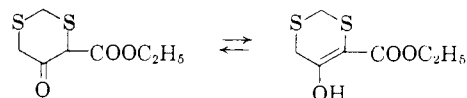
Oxidation of these heterocyclic compounds with hydrogen peroxide gave sulfoxides (XVIIIa, d) and sulfones (XIXa, d), depending on the amount of oxidizing agent used. The disulfone of the six-membered ketone (XIXa) was isolated as the hydrate, as shown by elemental analysis and extremely weak carbonyl absorption in the infrared. The ketal VIa was also oxidized to the corresponding disulfone which was soluble in dilute aqueous base.

In a study of the chemistry of 4-ethoxycarbonyl-5-*m*-dithianone (IIa), the existence of keto-enol forms was demonstrated. Thus, IIa was isolated from the reaction mixture as a pale yellow liquid, from which a solid slowly separated. The amount of solid could be increased by storing the product at 5° for several months. When a sample of the pure solid was distilled under reduced pressure and the distillate was cooled, partial crystallization

occurred. The solid and liquid were separated by filtration. Examination of the infrared and



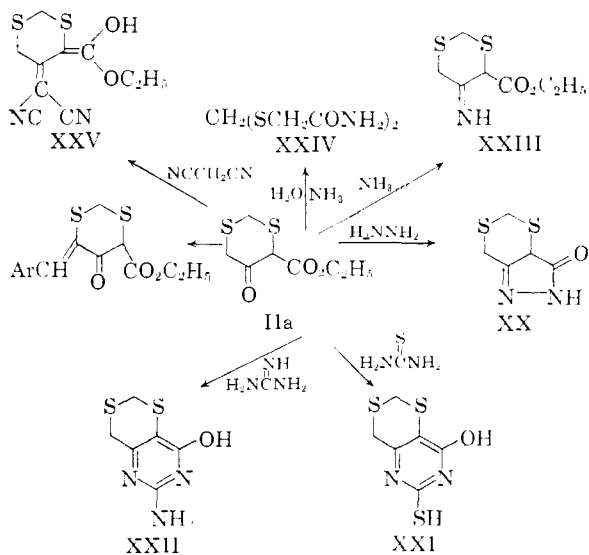
nuclear magnetic resonance spectra<sup>3</sup> of the solid and liquid indicated that they were tautomers, the liquid being the keto and the solid the enol form of IIa.



Determination of the acid strength of IIa gave a  $pK_A$  value of 9.2, which is comparable with those of phenol (9.9) and hydrogen cyanide (9.1). In contrast, the analogous 2-ethoxycarbonylcyclohexanone gave no measurable value under the same conditions.

In most of its chemical reactions, IIa behaves essentially as a  $\beta$ -keto ester. For example, it reacts with hydrazine to give a pyrazolone (XX), and with thiourea and guanidine to give pyrimidines (XXI, XXII).

Reaction of IIa of IIa with anhydrous ammonia gave the imino ester XXIIIk whereas reaction with aqueous ammonia caused cleavage of the ring to



(3) These results will be described in detail in a future publication from these laboratories.

(2) D. Vorlander and K. Kurze, *Ber.*, **59**, 2078 (1926).

XXIV, a result similar to those reported by Challenger.<sup>1</sup>

Malononitrile reacted with IIa to give a dicyanomethylene derivative. Examination of the infrared absorption spectrum of this product showed the absence of carbonyl group absorption. Accordingly, the compound is believed to exist as the enol XXV.

A series of highly colored monoarylidene derivatives was also prepared by reaction of IIa and IIc with aromatic aldehydes (Table I).

### Experimental

**Diethyl 3,5-dithiapimelate** has been prepared from ethyl mercaptoacetate and formaldehyde.<sup>4</sup> In a modification of this procedure, dry hydrogen chloride gas was passed through a mixture of 900 ml. of absolute ethyl alcohol, 368 g. (4 moles) of mercaptoacetic acid and 60 g. (2 moles) of formaldehyde. Distillation of the product gave a fraction (63 g., 18%), b.p. 75–76° (2.2 mm.),  $n_D^{25}$  1.4592, in addition to 344 g. (69%) of diethyl 3,5-dithiapimelate, b.p. 140° (0.5 mm.). The lower boiling product is apparently ethyl 3-thia-5-oxaheptanoate.

*Anal.* Calcd. for  $C_7H_{14}O_2S$ : S, 17.99; mol. wt., 178. Found: S, 18.28; mol. wt., 183.

By adding the ethyl alcohol to the mixture of mercaptoacetic acid, hydrogen chloride and formaldehyde, the formation of this by-product was eliminated.

A more convenient procedure is: A mixture of 500 ml. of toluene, 5 ml. of concentrated sulfuric acid and 380 g. (4 moles) of 97.1% mercaptoacetic acid was stirred and heated to 80°, and 158 g. (2 moles) of 37.8% aqueous formaldehyde was slowly added. During the addition, the temperature was maintained to give gentle reflux and reached 108° after 143 ml. of water had been removed. Over a period of one hour, 400 ml. of absolute ethyl alcohol was cautiously added at about 100°. Liquid was distilled from the reaction mixture until the temperature of the residue reached 120°. The residue was cooled, washed with 5% sodium hydroxide and water, dried and distilled to obtain 458 g. (91% yield) of product, b.p. 149–55° (1.5 mm.),  $n_D^{25}$  1.5020.

**4-Ethoxycarbonyl-5-*m*-dithianone (IIa).**—A solution of sodium ethoxide was prepared by adding 32.2 g. (1.40 gram-atoms) of sodium metal to 450 ml. of absolute ethyl alcohol. The mixture was diluted with 700 ml. of absolute ethyl ether, cooled to 10°, and 351 g. (1.40 moles) of diethyl 3,5-dithiapimelate was added. The stirred reaction mixture was kept at 5° for 8 hours, 25° for 10 hours, and then poured into a separatory funnel containing 170 ml. of concentrated hydrochloric acid and 1 kg. of ice and water. The organic layer was separated and the aqueous phase was extracted with five 500-ml. portions of ether. The volatile constituents were removed by heating the combined organic phase and extracts to 115° (8 mm.) to obtain 300 g. of a pale yellow, viscous oil from which 150 g. of IIa crystallized on cooling in an ice-bath. After storing the filtrate at 5° for a month, 25 g. more of IIa was isolated, constituting a total yield of 61% of the solid form, m.p. 62–64° when recrystallized from ethyl alcohol. The infrared absorption spectrum of the product showed a broad band at 3.0 to 3.75  $\mu$ , indicating hydrogen bonded OH, and three bands at 5.80, 6.05 and 6.30  $\mu$  in the carbonyl and double bond region. On the basis of these results, the solid is assigned the enol structure.

A sample of the recrystallized solid was distilled at 105° (0.2 mm.). The liquid distillate was cooled in ice and seeded with a crystal of the solid. Partial crystallization occurred. The liquid portion was separated by filtration, and its infrared absorption spectrum was determined immediately. The spectrum showed ester and ketone carbonyl bands at 4.75 and 5.85  $\mu$ , respectively, and no bands assignable for hydroxyl or carbon-carbon double bond absorption. Hence, this form is the ketoester.

**6-Ethoxycarbonyl-1,4-dioxo-7,8-dithiaspiro[4.5]decane (IIIa).**<sup>5</sup>—A mixture of 20.6 g. (0.1 mole) of IIa and 100 ml. of ethylene glycol was saturated with dry hydrogen chloride, heated on a steam-bath for one hour, cooled, and permitted

to stand overnight to obtain 23 g. of crystalline solid which, after recrystallization from ethyl alcohol, melted at 59–60°.

*Anal.* Calcd. for  $C_9H_{14}O_4S_2$ : C, 43.18; H, 5.64; S, 25.62. Found: C, 43.49; H, 5.76; S, 25.66.

**1,4-Dioxo-7,9-dithiaspiro[4.5]decane-6-carboxylic Acid (IVa).**—A solution of 2.5 g. (0.01 mole) of IIIa and 0.8 g. (0.02 mole) of sodium hydroxide in 25 ml. of water and 15 ml. of ethanol was stored at room temperature overnight, heated on a steam-bath for 5 hours to complete the saponification and to evaporate the alcohol, cooled, and acidified with concentrated hydrochloric acid. The solid which precipitated (2.0 g., 90% yield), was recrystallized from water, m.p. 200–201.5° with evolution of carbon dioxide.

*Anal.* Calcd. for  $C_7H_{10}O_4S_2$ : C, 37.83; H, 4.53; S, 28.85. Found: C, 38.19; H, 4.59; S, 29.07.

**5-*m*-Dithianone (Va).**<sup>6</sup>—A mixture of 50 ml. of water, 0.5 ml. of concentrated hydrochloric acid and 4 g. (0.018 mole) of IVa was heated on a steam-bath for 4 hours. Carbon dioxide was slowly liberated and the solid dissolved. A small amount of oil remained undissolved. The mixture was cooled in an ice-bath to obtain 2.3 g. (96% yield) of solid, m.p. 103–103.5° after two recrystallizations from water.

*Anal.* Calcd. for  $C_4H_6O_2S_2$ : C, 35.80; H, 4.51; S, 47.78. Found: C, 35.94; H, 4.96; S, 47.98.

An aqueous solution of Va gave a positive test with 2,4-dinitrophenylhydrazine reagent. The infrared spectrum of Va showed typical carbonyl absorption at 5.85  $\mu$ .

In another experiment, 133 g. (0.533 mole) of IIIa was converted to 61 g. (83%) of Va without isolating IVa.

**1,4-Dioxo-7,9-dithiaspiro[4.5]decane (VIa).**—Decarboxylation of IVa (4 g., 0.018 mole) was effected by heating at 140–170° for about one hour, or until no more carbon dioxide was evolved. The reaction mixture was cooled to obtain 3.0 g. (94%) of white solid, which was recrystallized from water, m.p. 105–105.5°.

*Anal.* Calcd. for  $C_8H_{10}O_2S_2$ : S, 35.96. Found: S, 36.30.

**8,8-Dimethyl-6-ethoxycarbonyl-1,4-dioxo-7,9-dithiaspiro[4.5]-decane (IIIb).**—Diethyl 4,4-dimethyl-3,5-dithiapimelate<sup>7</sup> was cyclized by the same procedure used for the preparation of IIa. The resulting cyclic  $\beta$ -ketoester was a liquid which could not be distilled without decomposition nor induced to crystallize. Accordingly, it was converted directly to the ketal as described for the preparation of IIIa. From 340 g. (1.2 moles) of the linear ester there was obtained 230 g. (68.5%) of free-flowing, white crystalline ketal, m.p. 76–77° after recrystallization from methanol.

*Anal.* Calcd. for  $C_{11}H_{18}O_3S_2$ : C, 47.46; H, 6.49; S, 23.03. Found: C, 47.65; H, 6.61; S, 22.86.

**8,8-Dimethyl-1,4-dioxo-7,9-dithiaspiro[4.5]decane-6-carboxylic Acid (IVb).**—Saponification of 161 g. (0.6 mole) of IIIb as described for IIIa gave 120 g. (89%) of solid product that was recrystallized from benzene, m.p. 114–115°.

*Anal.* Calcd. for  $C_9H_{14}O_4S_2$ : C, 43.18; H, 5.67; S, 25.87. Found: C, 43.34; H, 5.71; S, 25.87.

**2,2-Dimethyl-5-*m*-dithianone (Vb).**—A mixture of 100 ml. of water, 3 drops of concentrated hydrochloric acid and 25 g. (0.1 mole) of IVb was heated on the steam-bath for 15 hours. The product was isolated by extracting with ether, drying the extracts over anhydrous magnesium sulfate, and distilling; yield 12.1 g. (75%), b.p. 57.5–59° (0.5 mm.),  $n_D^{25}$  1.5540.

*Anal.* Calcd. for  $C_8H_{14}S_2O_2$ : C, 46.51; H, 6.84; S, 31.03. Found: C, 46.58; H, 6.99; S, 31.00.

**8,8-Dimethyl-1,4-dioxo-7,9-dithiaspiro[4.5]decane (VIb).**—Decarboxylation of 25.0 g. (0.1 mole) of IVb by heating at 122–140° gave a quantitative yield of product (20 g.) which melted at 76.5–77.5° after recrystallization from ethyl alcohol.

*Anal.* Calcd. for  $C_8H_{14}O_2S_2$ : C, 46.51; H, 6.84; S, 31.08. Found: C, 46.53; H, 6.96; S, 31.00.

**Diethyl 4-(*o*-chlorophenyl)-3,5-dithiapimelate (Ic)** was prepared by reaction of 211 g. (1.5 moles) of *o*-chlorobenzaldehyde and 360 g. (3 moles) of ethyl mercaptoacetate with anhydrous hydrogen chloride as a catalyst. The product was

(4) A. Tiberg, *Ber.*, **49**, 2026 (1916).

(5) E. G. Howard, U. S. Patent 2,790,810 (1957).

(6) E. G. Howard, U. S. Patent 2,790,811 (1957).

(7) R. L. Shriner, J. M. Cross and E. H. Dobraty, *THIS JOURNAL*, **61**, 2001 (1939).

isolated by washing the reaction mixture with aqueous base and with water, and drying. The clear, viscous liquid,  $n_D^{25}$  1.5512, could not be distilled; yield 447 g. (82%).

*Anal.* Calcd. for  $C_{18}H_{19}ClO_4S_2$ : S, 17.66; Cl, 9.77; mol. wt., 363. Found: S, 17.90; Cl, 9.52; mol. wt., 386.

**2-(*o*-Chlorophenyl)-4-ethoxycarbonyl-5-*m*-dithianone (IIc).**—To a cold solution of 1 mole of sodium ethoxide in 400 ml. of ethyl alcohol and 500 ml. of ether prepared by adding 23 g. (1 gram-atom) of sodium to 450 ml. of ethyl alcohol, was added 362.5 g. (1 mole) of Ic while maintaining the temperature of the reaction mixture at 0–3°. After 8 hours, the temperature was raised to 25° for 12 hours. The clear solution was added to a mixture of 500 g. of ice, 500 ml. of water and 120 ml. of concentrated hydrochloric acid. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to obtain 300 g. of a viscous, clear red liquid. A small sample was induced to crystallize by dissolving in ethyl alcohol, cooling the solution, and scratching the glass test-tube until crystals formed. These were used to seed the liquid product. Filtration yielded 175 g. (55%) of white solid, m.p. 48–49° after recrystallization from ethyl alcohol.

*Anal.* Calcd. for  $C_{18}H_{19}ClO_3S_2$ : Cl, 11.19; S, 20.24. Found: Cl, 11.52; S, 20.16.

**8-(*o*-Chlorophenyl)-6-ethoxycarbonyl-1,4-dioxo-7,9-dithiaspiro[4.5]decane (IIIc).**—The procedure employed for the synthesis of IIIa was used. From 152 g. (0.48 mole) of IIc, there was obtained 69 g. (55%) of product which melted at 120–121° after recrystallization from methanol.

*Anal.* Calcd. for  $C_{16}H_{17}ClO_4S_2$ : C, 49.92; H, 4.75; S, 17.77. Found: C, 50.15; H, 4.78; S, 17.72.

**8-(*o*-Chlorophenyl)-1,4-dioxo-7,9-dithiaspiro[4.5]decane-6-carboxylic Acid (IVc).**—The method was essentially that used in the synthesis of IVa starting with 72 g. (0.2 mole) of IIIc. Before the reaction mixture was acidified, 5 g. of the sodium salt of the acid precipitated. A sample was recrystallized from water, m.p. 269–272.5° dec.

*Anal.* Calcd. for  $C_{15}H_{12}ClNaO_4S_2$ : Na, 6.5; S, 18.07. Found: Na, 6.5; S, 18.13.

Acidification of the reaction mixture from which the sodium salt precipitated gave 61 g. of hard amorphous solid, which appeared to be a mixture of stereoisomers. Recrystallization from ethyl alcohol gave 15 g. of solid, m.p. 190–193° dec. The total yield of sodium salt and mixture of crude isomeric acids was quantitative.

*Anal.* Calcd. for  $C_{15}H_{13}ClO_4S$ : S, 19.26. Found: S, 18.91.

**2-(*o*-Chlorophenyl)-5-*m*-dithianone (Vc).**—In the manner described for the synthesis of Va, 12.5 g. (0.038 mole) of IVc gave 8.5 g. (92%) of product which was recrystallized from methanol, m.p. 140–140.5°.

*Anal.* Calcd. for  $C_{10}H_9ClO_2S_2$ : C, 49.07; H, 3.71; Cl, 14.49; S, 26.20. Found: C, 49.34; H, 3.81; Cl, 14.57; S, 25.98.

**8-(*o*-Chlorophenyl)-1,4-dioxo-7,9-dithiaspiro[4.5]decane (VIc).**—Decarboxylation of 46 g. (0.108 mole) of the crude acid IVc gave 11.5 g. (37%) of product which was recrystallized from methanol, m.p. 120–124°.

*Anal.* Calcd. for  $C_{12}H_{13}ClO_2S_2$ : C, 49.90; H, 4.54; Cl, 12.26; S, 22.20. Found: C, 49.91; H, 4.65; Cl, 12.41; S, 22.39.

**1,4-Dioxo-7,9-dithiaspiro[4.5]decane-7,7,9,9-tetraoxide.**—To a solution of 1.78 g. (0.01 mole) of compound VIa was added 5.1 g. (0.045 mole) of 30% aqueous hydrogen peroxide over a period of 4 hours. The reaction mixture was allowed to stand for 4 days and poured into water to obtain 2.20 g. of a white amorphous solid. The solid was purified by dissolving in water containing a little base and reprecipitating with dilute hydrochloric acid, m.p. 330° with sublimation.

*Anal.* Calcd. for  $C_8H_{10}O_8S_2$ : C, 29.75; H, 4.16. Found: C, 30.29; H, 4.35.

**8,8-Dimethyl-6-ethoxycarbonyl-1,4-dioxo-7,9-dithiaspiro[4.5]decane-7,7,9,9-tetraoxide.**—The same method was employed as described above. From 2.78 g. (0.01 mole) of IIIb was isolated 2.5 g. of disulfone which, after recrystallization from ethyl alcohol, melted at 153–154°.

*Anal.* Calcd. for  $C_{11}H_{18}O_8S_2$ : C, 38.59; H, 5.30; S, 18.73. Found: C, 38.47; H, 5.38; S, 18.61.

**1,4-Dithiacycloheptan-6-one (VII).**—Solutions of the reactants were prepared: Solution A, after 55.3 g. (2.4 gram-atoms) of sodium had reacted with 700 ml. of absolute methanol in a 1-l. volumetric flask to which a condenser had been attached, 113 g. (1.2 moles) of 1,2-ethanedithiol was added. The volume was brought to 1 l. with methanol. Solution B: *sym*-Dichloroacetone (152 g., 1.2 moles) was dissolved in about 600 ml. of absolute ether and enough ether was added to bring the volume to 1 l.

These two solutions were added at a rate of 100 ml. each for the first hour, 150 ml. each for the second hour and the remainder at 250 ml. each per hour to a mixture of 250 ml. each of methanol and absolute ether. The reaction vessel and solution A were blanketed with oxygen-free nitrogen. The temperature of the reaction was maintained at 10°. The reaction mixture was poured into an ice-water-ether mixture containing 50 ml. of 10% sodium hydroxide. The aqueous phase was extracted with three 100-ml. portions of ether. The small amount of polymer that separated was removed by decantation. This synthesis was carried out three times and the combined extracts were distilled after removal of the ether to obtain 366 g. (70%) of product, b.p. 85–90° (0.3 mm.),  $n_D^{25}$  1.5925.

*Anal.* Calcd. for  $C_6H_8OS_2$ : C, 40.51; H, 5.44; S, 43.26; mol. wt., 148. Found: C, 40.78; H, 5.44; S, 43.17; mol. wt., 158.

In later experiments, it was found that the reaction could be carried out in water without lowering the yield of product.

Compound VII was slightly soluble in water and gave a ketone test with 2,4-dinitrophenylhydrazine reagent. Nuclear magnetic resonance measurements showed the presence of equal amounts of two kind of hydrogen, in keeping with the proposed structure. Its infrared absorption spectrum had a typical carbonyl band at 5.85  $\mu$ .

**1,5-Dithiacyclooctan-3-one (VIII).**—By the same procedure as that described above, reaction of 24.6 g. (0.2 mole) of *sym*-dichloroacetone and 21.6 g. (0.2 mole) of 1,3-propanedithiol<sup>8</sup> gave 10.4 g. (32%) of product, b.p. 84–93° (0.35 mm.),  $n_D^{25}$  1.5813, which crystallized on cooling. The product melting at 46–47° after recrystallization from ethyl alcohol. The infrared absorption spectrum showed a typical ketone carbonyl band at 5.88  $\mu$ .

*Anal.* Calcd. for  $C_6H_{10}OS_2$ : C, 44.41; H, 6.21; S, 39.52; mol. wt., 162. Found: C, 44.61; H, 6.20; S, 39.65; mol. wt., 161, 163.

**1,4-Dioxo-7,12-dithiaspiro[4.8]tridecane (Ethylene Glycol Ketal of IX).**—By the method described for the synthesis of VII, reaction of 24.6 g. (0.2 mole) of *sym*-dichloroacetone and 26.4 g. (0.2 mole) of 1,4-butanedithiol<sup>8</sup> gave solid polymer as the major product. The solid was removed by filtration and the filtrate was distilled to obtain 4 g. of an oil, b.p. 93–100° (0.3 mm.). Reaction of the oil with ethylene glycol using anhydrous hydrogen chloride as a catalyst gave the ketal which was recrystallized from ethyl alcohol, m.p. 136.5–138°. The over-all yield of ketal was 1.1 g. (2.5%).

*Anal.* Calcd. for  $C_9H_{14}O_2S_2$ : C, 49.09; H, 7.32; S, 29.10; mol. wt., 220. Found: C, 48.85; H, 7.36; S, 29.09; mol. wt., 220.

**Reaction Product of 5-*m*-Dithianone and Salicylaldehyde (X).**—A solution of 2.68 g. (0.02 mole) of Va, 4.88 g. (0.04 mole) of salicylaldehyde and five drops of piperidine in 70 ml. of absolute ethyl alcohol was stored at room temperature for five months to obtain one large crystal which weighed 1.3 g. (20%), m.p. 224–225° after recrystallization from ethyl alcohol. The infrared spectrum showed no absorption in the hydroxyl region. A band in the carbonyl region at 5.65  $\mu$  was extremely weak.

*Anal.* Calcd. for  $C_{13}H_{12}O_2S_2$ : C, 66.64; H, 3.73; S, 19.77. Found: C, 66.77; H, 4.03; S, 19.94.

This procedure was used to prepare the products summarized in Table I.<sup>9</sup> The reactions required from one day to several months for completion.

**5-Dicyanomethylene-1,3-dithiane (IXa).**—A solution prepared by warming 1.34 g. (0.01 mole) of Va in a mixture of 40 ml. of ethyl alcohol and 25 ml. of water was cooled to 30° and 0.66 g. (0.01 mole) of malononitrile was added. In a few minutes, a white solid began to form. The mixture was

(8) E. E. Reid, *J. Am. Chem. Soc.*, **65**, 1466 (1943).

(9) We are indebted to Dr. Darwin D. Davis for a number of these preparations.

warmed to 40°, permitted to cool slowly, and allowed to stand at room temperature for four days. Filtration gave 1.80 g. (99%) of cream colored crystalline solid, m.p. 179–180.5° after recrystallization from ethyl alcohol.

*Anal.* Calcd. for  $C_7H_8N_2S_2$ : C, 46.13; H, 3.32; N, 15.44; S, 35.18. Found: C, 46.42; H, 3.50; N, 15.47; S, 35.43.

**6-Dicyanomethylene-1,4-dithiacycloheptane (XId).**—A solution of 14.8 g. (0.1 mole) of VII, 6.6 g. (0.1 mole) malononitrile and 25 ml. of absolute ethyl alcohol was stored at room temperature for 19 days to obtain a quantitative yield (19.5 g.) of white crystalline solid melting at 167–168° after recrystallization from ethyl alcohol.

*Anal.* Calcd. for  $C_8H_8N_2S_2$ : C, 48.95; H, 4.11; N, 14.28; S, 32.67. Found: C, 49.11; H, 4.21; N, 14.33; S, 32.67.

**5-*m*-Dithianone Oxime (XII).**—A solution of 5.34 g. (0.04 mole) of Va in 50 ml. of methanol and 50 ml. of water was heated on a steam-bath, and 3.46 g. (0.05 mole) of hydroxylamine hydrochloride was added. When solution was complete, 6.80 g. (0.05 mole) of sodium acetate trihydrate in 10 ml. of water was added. The mixture was filtered immediately and cooled slowly to obtain 4.00 g. (69%) of white solid. The product was recrystallized from a water-alcohol mixture; m.p. 166–167°.

*Anal.* Calcd. for  $C_4H_7NOS_2$ : C, 32.19; H, 4.73; N, 42.97; S, 9.39. Found: C, 32.42; H, 4.80; S, 43.13; N, 9.42.

**5-*m*-Dithiylamine (XIII).**—A procedure adapted from that described by Walter<sup>10</sup> was used for the reduction of the oxime with lithium aluminum hydride. A mixture of 100 ml. of absolute ether and 3.8 g. (0.1 mole) of lithium aluminum hydride was stirred and blanketed with nitrogen. A solution of 3.18 g. (0.0214 mole) of XII in 25 ml. of purified tetrahydrofuran was added cautiously. After the addition was complete, the mixture was refluxed and stirred for 7 hours. The lithium aluminum hydride was destroyed by cautiously adding a mixture of water, ethyl alcohol and ether. The white reaction mixture was filtered, and the solids were washed with ether. The ether was removed from the filtrate by distillation under reduced pressure to obtain a pale yellow solid which, after recrystallization from petroleum ether, weighed 1.5 g. (52%) and melted at 78–79° with sublimation beginning at about 50°.

*Anal.* Calcd. for  $C_4H_9NS_2$ : N, 10.36; S, 47.71. Found: N, 10.07; S, 47.04.

**5,5-Bis-(*p*-hydroxyphenyl)-*m*-dithiane (XIVa).**—A mixture of 13.4 g. (0.1 mole) of Va, 28.2 g. (0.3 mole) of phenol and 30 ml. of concentrated hydrochloric acid was stored at room temperature for one day. The solid product was washed with hot water to remove unreacted phenol. The resulting sticky, pale pink solid was recrystallized from acetonitrile, m.p. 109°.

*Anal.* Calcd. for  $C_{16}H_{18}O_2S_2 \cdot H_2O$ : S, 19.89. Found: S, 20.05.

**6,6-Bis-(*p*-hydroxyphenyl)-1,4-dithiacycloheptane (XIVd).**—A mixture of 1.48 g. (0.1 mole) of VII, 2.4 g. (0.025 mole) of phenol and 2 ml. of concentrated hydrochloric acid was stored at room temperature for two days with occasional shaking to obtain a pale purple-colored mass. Addition of water gave a white paste from which a solid was obtained by treatment with benzene. After recrystallization from benzene, the solid melted at 130–134° with evolution of benzene, resolidified, and finally melted at 186–187°. The analytical sample was recrystallized from toluene and dried at 140° (1 mm.).

*Anal.* Calcd. for  $C_{17}H_{18}O_2S_2$ : C, 64.12; H, 5.70; S, 20.14. Found: C, 64.13; H, 5.93; S, 19.57.

**1,4-Dioxa-7,10-dithiaspiro[4.6]undecane (XV).**—One gram of VII was suspended in a few ml. of dry ethylene glycol and dry hydrogen chloride gas was added. The temperature rose sharply and a mass of crystalline solid formed, m.p. 101° after recrystallization from ethyl alcohol.

*Anal.* Calcd. for  $C_7H_{12}O_2S_2$ : C, 43.72; H, 6.29; S, 33.34. Found: C, 44.03; H, 6.34; S, 33.62.

**1,4,7,10-Tetrathiaspiro[4.6]undecane (XVI).**—Dry hydrogen chloride was bubbled through a mixture of 1 g. of VII and 2 g. of 1,2-ethanedithiol. When benzene was added, a

white solid began to form. Evaporation of the solvent left a pasty solid which was pressed dry on filter paper and recrystallized from benzene, m.p. 140°.

*Anal.* Calcd. for  $C_6H_{12}S_4$ : C, 37.46; H, 5.49; S, 57.28. Found: C, 37.89; H, 5.39; S, 56.88.

**1,4-Dithia-7,9-diazaspiro[4.6]undecan-8,10-dione (XVII).**—To a stirred mixture of 14.8 g. (0.1 mole) of VII, 50 ml. of ethyl alcohol, 22.8 g. (0.2 mole) of ammonium carbonate monohydrate and 25 ml. of water at 60° was added dropwise over 45 minutes a solution of 4.9 g. (0.1 mole) of sodium cyanide in 15 ml. of water. Heating and stirring were continued for 4 hours. The solid product was isolated by pouring the reaction mixture into cold water and cooling; weight 14.8 g. (68%). The sample was purified by dissolving in water containing a small quantity of sodium hydroxide, treating with decolorizing carbon, filtering, and acidifying the filtrate with dilute hydrochloric acid, m.p. 294–294.5°.

*Anal.* Calcd. for  $C_7H_{10}N_2O_2S_2$ : C, 38.51; H, 4.62; N, 12.84; S, 29.37. Found: C, 38.77; H, 4.52; N, 13.00; S, 30.46.

**5-Oxo-*m*-dithiane-1,3-dioxide (XVIIIa).**—To a solution of 1.34 g. (0.01 mole) of Va in 30 ml. of acetic acid was added dropwise over a period of 3 hours, 2.3 g. (0.02 mole) of hydrogen peroxide. The temperature rose from 28 to 31°. The reaction mixture was permitted to stand for one hour, during which time a small amount of solid precipitated, and was poured into a mixture of 100 ml. each of ether and petroleum ether to obtain a sticky solid that became powdery when washed with water. A sample was recrystallized by placing the impure material on a filter funnel, pouring hot water over it, and cooling the filtrate immediately. The infrared absorption spectrum exhibited a doublet band at 9.45 and 9.8  $\mu$  which is characteristic of sulfoxides. A band at 5.90  $\mu$  was due to the carbonyl group.

*Anal.* Calcd. for  $C_4H_8O_3S_2$ : S, 38.58. Found: S, 38.80.

**6-Oxo-1,4-dithiacycloheptane-1,4-dioxide (XVIIId).**—To a solution of 4.4 g. (0.03 mole) of VII in 25 ml. of acetic acid was added 6.9 g. (0.06 mole) of 30% hydrogen peroxide while the temperature was kept below 34°. The mixture was allowed to stand for five days. Ether was added to bring about the precipitation of 3.0 g. of solid, which was recrystallized from ethyl alcohol, m.p. 177–181° dec. Absorption bands at 9.75 and 9.85  $\mu$  in the infrared spectrum indicate the presence of the sulfoxide groups. Normal carbonyl absorption occurred at 5.90  $\mu$ . No bands in the sulfone region were present.

*Anal.* Calcd. for  $C_4H_8O_3S_2$ : C, 33.32; H, 4.47; S, 35.58. Found: C, 33.30; H, 4.50; S, 35.45.

**5,5-Dihydroxy-1,3-dithiane-1,1,3,3-tetraoxide (XIXa).**—To a solution of 1.34 g. (0.01 mole) of Va in 30 ml. of acetic acid was added 5.1 g. (0.045 mole) of 30% hydrogen peroxide in water over a period of 4 hours. After four days, 0.75 g. of solid was collected. Recrystallization from water gave a white amorphous powder which melted at 260–265° with vigorous decomposition. Typical hydroxy bands were found in the infrared absorption spectrum at 2.95  $\mu$  and an exceptionally weak band was found in the carbonyl area at 5.75  $\mu$ . These results suggest a dihydroxy structure rather than that of a simple hydrate.

*Anal.* Calcd. for  $C_4H_8O_6S_2$ : S, 29.65. Found: S, 29.80.

**6-Oxo-1,4-dithiacycloheptane-1,1,4,4-tetraoxide (XIXd).**—To a solution of 4.4 g. (0.03 mole) of VII in 25 ml. of acetic acid was added 13.8 g. (0.12 mole) of 30% hydrogen peroxide while the temperature was kept below 34°. The solid (4.8 g.) that formed after the mixture had been allowed to stand for five days was recrystallized from water, m.p. 279–282°. Triple bands in the infrared absorption spectrum at 7.55, 7.65 and 7.75  $\mu$ , as well as a band at 9.00  $\mu$ , are indicative of the sulfone groups. A carbonyl band was present at 5.80  $\mu$ .

*Anal.* Calcd. for  $C_6H_8O_6S_2$ : C, 28.30; H, 3.80; S, 30.21. Found: C, 28.20; H, 3.77; S, 30.66.

**Reaction of IIa with Aqueous Ammonia.**—A solution of 2.06 g. (0.01 mole) of IIa in 15 ml. of concentrated aqueous ammonia was allowed to stand for 2 hours to obtain 1.65 g. (85%) of 3,5-dithiapimelamide (XXIV), m.p. 172–173° after recrystallization from ethyl alcohol.

(10) C. W. Walter, Jr., *THIS JOURNAL*, **74**, 5185 (1952).

*Anal.* Calcd. for  $C_8H_{10}O_2N_2S_2$ : N, 14.42; S, 33.01. Found: N, 14.43; S, 32.80.

**6,7a-Dihydro-*m*-dithiino[5,4-*c*]pyrazol-7(4H)one (XX).**—To a mixture of 10.3 g. (0.05 mole) of IIa and 50 ml. of ethyl alcohol at reflux temperature was added 2.5 g. (0.05 mole) of hydrazine hydrate. A vigorous reaction occurred and the product precipitated in quantitative yield (8.7 g.). After recrystallization from ethyl alcohol, it melted at 233–236° with decomposition beginning at 220°.

*Anal.* Calcd. for  $C_8H_8N_2OS_2$ : C, 34.46; H, 3.47; S, 36.80. Found: C, 34.41; H, 3.62; S, 36.96.

**6-Thio-*m*-dithiano[5,4-*d*]uracil (XXI).**—A solution of 30 ml. of ethyl alcohol, 0.02 mole of sodium ethoxide, 2.06 g. (0.01 mole) of IIa and 0.76 g. (0.01 mole) of thiourea was refluxed for 4 hours, and poured into water. The solid (0.56 g.) was collected on a filter and purified by dissolving in 1% cold sodium hydroxide, treating with decolorizing carbon and acidifying. It did not melt below 300°.

*Anal.* Calcd. for  $C_8H_8N_2OS_2$ : C, 33.01; H, 2.77; N, 12.84; S, 44.06. Found: C, 33.12; H, 2.83; N, 12.83; S, 44.02.

**6-Amino-*m*-dithiano[5,4-*d*]pyrimidin-8-ol (XXII).**—A clear solution of 0.035 mole of sodium ethoxide, 2.06 g. of IIa and 1.18 g. (0.01 mole) of guanidinium thiocyanate in 30 ml. of ethyl alcohol was stirred at reflux for 4 hours, poured into a mixture of ice and water, and neutralized with hydrochloric acid. The solid product (1.0 g.) was purified by dissolving in aqueous base, treating with decolorizing carbon, and precipitating by acidification. When heated, the solid began to decompose at 220° but did not melt at temperatures up to 300°.

*Anal.* Calcd. for  $C_8H_8N_3OS_2$ : C, 35.80; H, 3.51; S, 31.86. Found: C, 35.89; H, 3.70; S, 31.80.

**2-(*o*-Chlorophenyl)-6,7a-dihydro-*m*-dithiino[5,4-*c*]pyrazol-7(4H)one.**—A solution of 19 g. (0.06 mole) of 2-(*o*-chlorophenyl)-4-ethoxycarbonyl-5-*m*-dithianone and 3 g. (0.06 mole) of hydrazine hydrate in 16 ml. of methanol was heated on a steam-bath for about three minutes, and cooled in an ice-bath. The white solid product (17 g.) was collected by filtration and recrystallized from a water-methanol mixture, m.p. 234–238° dec.

*Anal.* Calcd. for  $C_{11}H_9ClN_2OS_2$ : Cl, 12.45; S, 22.52; N, 9.84. Found: Cl, 12.90; S, 22.56; N, 9.72.

**4-Ethoxycarbonyl-5-*m*-dithianimine (XXIII).**—Dry ammonia was passed through a suspension of 61.8 g. (0.3 mole) of IIa in 120 ml. of absolute ethyl alcohol at 25°. The ester dissolved and a crystalline solid suddenly precipitated. The solid was collected by filtration and dissolved in warm ethyl alcohol. The solution was cooled to 30°,

rapidly saturated with dry ammonia gas, and cooled to 5° overnight to obtain 29 g. (47%) of product, m.p. 122–123.5°.

*Anal.* Calcd. for  $C_7H_{11}NO_2$ : C, 40.95; H, 5.40; S, 31.23; N, 6.82. Found: C, 40.69; H, 5.69; S, 31.19; N, 7.16.

The infrared absorption spectrum has bands at 2.92 and 3.02  $\mu$  in the N-H region and at 6.1  $\mu$  where carbonyl and imino double bonds show characteristic absorption.

When the product was not isolated from the reaction mixture in a short time, it was converted to 3,5-dithiapimelamide by the water formed in the reaction.

**5-Dicyanomethylene-4-ethoxyhydroxymethylene-*m*-dithiane (XXV).**—To a solution of 20.6 g. (0.1 mole) of IIa in a mixture of 70 ml. of ethyl alcohol and 40 ml. of water at 60° was added 6.6 g. (0.1 mole) of malononitrile. The mixture was cooled to room temperature to obtain 3 g. of a gummy yellow solid, which melted at 195–197° after it was washed with benzene and recrystallized from a mixture of ethyl alcohol and water. The structure assignment is based on the presence of the OH absorption band in the infrared spectrum at 3.2  $\mu$  and the absence of typical ester carbonyl band. Bands at 4.5  $\mu$  and at 6.25 and 6.4  $\mu$  indicate the presence of a conjugated nitrile group and carbon-carbon unsaturation.

*Anal.* Calcd. for  $C_{10}H_{10}N_2O_2S_2$ : C, 47.22; H, 3.96; S, 25.21; N, 11.16. Found: C, 47.35; H, 4.14; S, 25.41; N, 11.16.

**1,4-Dioxa-7,9-dithiaspiro[4.5]decane-6-carboxylic Acid Chloride (XXVI).**—A stirred mixture of 22.2 g. (0.1 mole) of IVa and 45.3 g. (0.30 mole) of thionyl chloride was heated at 37–39° until sulfur dioxide and hydrogen chloride no longer were evolved. The resulting clear yellow solution was stored overnight at room temperature. Excess thionyl chloride was removed by vacuum distillation to obtain 23.5 g. of product, which, after two recrystallizations from anhydrous benzene, melted at 91–91.5°.

*Anal.* Calcd. for  $C_7H_7ClO_3S$ : S, 26.64; Cl, 14.73. Found: S, 26.84; Cl, 14.84.

**1,4-Dioxa-7,9-dithiaspiro[4.5]decane-6-carboxamide (XXVII).**—A sample of the acid chloride was dissolved in benzene to which was added a large excess of ammonia in ether solution. The mixture was stirred for one-half hour and the solvent removed by evaporation at room temperature. The ammonium chloride was extracted from the residue with water and a portion of the remaining solid was recrystallized from ethyl alcohol, m.p. 179.5–181°.

*Anal.* Calcd. for  $C_7H_{11}O_3NS_2$ : C, 37.99; H, 5.01; N, 6.33; S, 28.98. Found: C, 38.37; H, 5.20; N, 6.33; S, 29.10.

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## 2,2,5,5-Tetramethyl-1,4-diazabicyclo[2.2.2]octane Methochloride

BY S. M. McELVAIN AND THOMAS A. LIES<sup>1</sup>

RECEIVED JUNE 1, 1959

The bicyclic structure named in the title was prepared by the intramolecular displacement of the halogen of 2,2,5,5-tetramethyl-1-(2-chloroethyl)-piperazine methochloride (VIII) by the 4-nitrogen. Attempts to demethylate this quaternary salt to yield the bicyclic ditertiary amine IV were unsuccessful.

Earlier work in this Laboratory showed that the formation of the bicyclo structure IV by the establishment of a 1,4-ethylene bridge *via* an intramolecular displacement of the halogen of a 1 - (2 - haloethyl) - 2,2,5,5 - tetramethylpiperazine (I) was not feasible. Pryde<sup>2</sup> found that the free base I (X = Cl or Br) preferentially formed the

(1) Standard Oil Foundation Fellow 1955–1956; Wisconsin Alumni Research Foundation Research Assistant 1956–1958; du Pont Summer Research Assistant 1957.

(2) S. M. McElvain and E. H. Pryde, *THIS JOURNAL*, **71**, 326 (1949).

ethylene immonium cation II, which either underwent self-condensation to form polymers or was hydrolyzed to the 1-hydroxyethyl derivative III. Bannister<sup>3</sup> was able to prepare the bicyclic amine IV in only 0.15–0.5% yields by the pyrolysis of the dihydrobromide salt of I (X = Br).

The purpose of the present work was to determine whether an ethylene bridge could be established from a structure of the type of I if the tertiary nitrogen were first quaternized to prevent the for-

(3) S. M. McElvain and L. A. Bannister, *ibid.*, **76**, 1126 (1954).