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gem-Dithiols[1]

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gem-Dithiols, $R_2C(SH)_2$, have been prepared and isolated as chemical entities for the first time. They are formed, along with polysulfides, when aldehydes or ketones are heated with hydrogen sulfide under pressure. The structures of the *gem*-dithiols were established by diacylation to $R_2C(SCOR')_2$, dialkylation to $R_2C(SR')_2$, reduction to R_2CHSH, and hydrolysis to the parent aldehyde or ketone. Other properties of the *gem*-dithiols are also described.

gem-Dithiols are compounds of the general formula $R_2C(SH)_2$. It appears that no member of this class has been isolated before now. Baumann[2] treated neutral, aqueous formaldehyde with hydrogen sulfide and by methylation and oxidation of an ether-extractable oil obtained $CH_2(SO_2CH_3)_2$, a derivative of methanedithiol, but he did not isolate methanedithiol itself. Mitchell, Ott and Reid[3] reduced carbon disulfide with zinc and acetic acid and isolated heavy-metal salts believed to be derivatives of $CH_2(SCSSH)_2$, the condensation product of two molecules of carbon disulfide with one of methanedithiol, but they were unable to isolate methanedithiol. Farlow and Signaigo[4] suggested that *gem*-dithiols might be intermediates in the catalytic conversion of aldehydes and ketones to mercaptans by hydrogen and either sulfur or hydrogen sulfide under pressure, but did not isolate any such intermediate in a pure state. Kelber and Schwarz[5] condensed aryl methyl ketones with carbon disulfide under the influence of potassium hydroxide and obtained β-ketocarbodithioic acids, which in several reactions behaved as the enthiolic *gem*-dithiols, $ArCOCH{=}C(SH)_2$.

TABLE 1

PRODUCTS OBTAINED BY TREATING ALDEHYDES AND KETONES WITH HYDROGEN SULFIDE

Aldehyde or ketone	Temp., °C.	Pressure, atm.	Time, hours	Method	Products isolated (with % yields)
Formaldehyde^d	42	30	16	A^a	Methanedithiol (33)
Propionaldehyde	30	540–1070	15	C	1,1-Propanedithiol (21); propyl disulfide (13); propyl trisulfide (28)
Propionaldehyde	80	50	15	A^a	1,1-Propanedithiol (16); propyl disulfide (23); propyl polysulfides (*ca.* 40)
Benzaldehyde	50	35	15	A^a	Benzaldehyde (66); α-2,4,6-triphenyltrithiane (3); β-2,4,6-triphenyltrithiane (4)
Benzaldehyde	75	50	15	A^a	Benzaldehyde (49); phenylmethanedithiol (17)
Benzaldehyde	80	7900–8500	14	C	Benzyl disulfide (9); benzyl polysulfides (*ca.* 40)
3,5,5-Trimethylhexanal	50	35	15	A	Water (78); 3,5,5-trimethylhexanal (31); 3,5,5-trimethyl-1,1-hexanedithiol (26)
Acetone	30	7500–8500	15	C	2,2-Propanedithiol (26); isopropyl disulfide (5)
Acetone	80	7500–8500	15	C	Isopropyl disulfide (50); isopropyl tetrasulfide (11)
Acetone	125	500–1500	15	C	Isopropyl disulfide (33); isopropyl trisulfide (10); isopropyl tetrasulfide (10)
Acetone	125	70	15	A^a	2,2-Propanedithol (7)
Diethyl ketone	30	7000–8500	65	C	3,3-Pentanedithiol (38)
Cyclohexanone	30	7500–8500	15	C^c	1,1-Cyclohexanedithiol (65)
Cyclohexanone	30	700–1000	15	B	Cyclohexanone (40); 1,1-cyclohexanedithiol (38)
Cyclohexanone	130	900–1000	2	B	Cyclohexanone (13); 1,1-cyclohexanedithiol (6); cyclohexyl disulfide (63)
Cyclohexanone	110	65	10	A^a	Cyclohexanone (80); 1,1-cyclohexanedithiol (4)
Acetophenone	50	7500–8500	14	C	1-Phenyl-1,1-ethanedithiol (3)^{b,c}
d,l-Camphor	80	8000–8500	14	C	2,2-Camphanedithiol (6)^{b,c}
12-Tricosanone	30	7500–8500	18	C	12,12-Tricosanedithiol (3)^{b,c}
Acetonylacetone	80	7500–8500	15	C	*gem*-dithiols (trace)^c; $CH_3CHCH_2CH_2CH(CH_3)SS$ (9); $CH_3CHCH_2CH_2CH(CH_3)SSS$ (25)

^{a} Reaction vessel was a 1-l. stainless-steel rocker-bomb. ^{b} Most of the ketone did not react. The *gem*-dithiol was not isolated; its yield is based on a titration with iodine after removal of hydrogen sulfide and ether from the ether extract. ^{c} The *gem*-dithiol test with lead acetate was positive. ^{d} Technical 37% aqueous formaldehyde was used.

gem-Dithiols have now been isolated as a result of a study of the interaction of aldehydes and ketones with hydrogen sulfide at pressures between

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[1] Presented before the Organic Division of the American Chemical Society at Milwaukee, Wisconsin, on April 1, 1952.

[2] E. Baumann, *Ber.*, **23**, 1869 (1890).

[3] J. A. Mitchell, E. Ott and E. E. Reid, *Ind. Eng. Chem.*, **23**, 694 (1931).

[4] M. W. Farlow and F. K. Signaigo (to E. I. du Pont de Nemours & Company), U. S. Patents 2,402,613 and 2,402,615 (1946).

[5] C. Kelber and A. Schwarz, *Ber.*, **43**, 1252 (1910); **44**, 1693 (1911); **45**, 137 (1912).

35 and 8500 atmospheres. They are formed in accordance with the equations

$$RCHO + 2H_2S \longrightarrow RCH(SH)_2 + H_2O$$

$$R_2CO + 2H_2S \longrightarrow R_2C(SH)_2 + H_2O$$

Some of the *gem*-dithiols can be obtained so easily that it is surprising none has been previously reported. It is only necessary to agitate an aldehyde or ketone with excess hydrogen sulfide at a suitable temperature and pressure, no catalyst being required. Well-characterized *gem*-dithiols were obtained from formaldehyde, propionaldehyde, 3,5,5-trimethylhexanal, benzaldehyde, acetone, diethyl ketone and cyclohexanone. There was evidence that several other substances, including 12-tricosanone, *d,l*-camphor and acetophenone, can be converted to *gem*-dithiols, although the *gem*-dithiols were not isolated in these cases. The reaction is therefore quite general. In the best cases yields were as high as 65%, but they were more often 15–35%. A competing reaction, the formation of polysulfides, was a common cause of low yields.

$$R_2CO \xrightarrow{H_2S} H_2O + (R_2CH)_2S_x \quad (x = 2\text{–}4)$$

The conditions and products of twenty representative experiments in which aldehydes or ketones were treated with hydrogen sulfide are listed in Table I. On the basis of the experience gained in these and over seventy other experiments, the following statements can be made about the effect of reaction conditions on *gem*-dithiol formation. Ketones undergo the reaction less readily than aldehydes, and sterically-hindered ketones are still less reactive. The reaction is favored by high ratios of hydrogen sulfide to carbonyl compound. The reaction is little affected by the presence of a strong acid such as *p*-toluenesulfonic acid, of a weak acid such as acetic acid, or of water, but a base such as triethylamine greatly favors the formation of high-boiling material at the expense of *gem*-dithiol. For a given carbonyl compound and ratio of components there exist optimum sets of temperature, pressure and reaction time; by increasing any one of the three variables there results a lower yield of *gem*-dithiol because of increased polysulfide formation, and by decreasing any one of them there results a lower yield of *gem*-dithiol because less carbonyl compound reacts. The carbonyl compounds differ so much in reactivity toward hydrogen sulfide, and so many factors affect the yield, that many experiments are usually needed to find the best conditions for preparing a given *gem*-dithiol. Conditions that give the best yield are not always the most practical; for example, the best yield may require a pressure of over 1000 atmospheres.

Physical Properties of *gem*-Dithiols.—The seven *gem*-dithiols that have been well characterized are colorless, distillable liquids with odors that are unpleasant in varying degrees. Methanedithiol and 1,1-propanedithiol have powerful, onion-like odors that in our opinion are strikingly more offensive than the odor of any of the common mercaptans. 3,5,5-Trimethyl-1,1-hexanedithiol, with the highest molecular weight of the seven, has a slight odor which is only mildly objectionable. The odors of the other four lie between these extremes.[6]

The *gem*-dithiols are, considering their structure, remarkably stable substances. Thus, a small quantity (5 g.) of 1,1-propanedithiol can be distilled at atmospheric pressure (b.p. 142°) without appreciable decomposition. The other *gem*-dithiols studied, although less stable under conditions of distillation, suffer little decomposition when distilled at pressures that give boiling points between 60 and 80°. They can partially withstand the conditions of steam distillation. For instance, half of a 27-g. batch of 3,5,5-trimethyl-1,1-hexanedithiol survived steam distillation. 1,1-Propanedithiol, 1,1-cyclohexanedithiol and 3,5,5-trimethyl-1,1-hexanedithiol can be stored in brown bottles at room temperature for at least a year without appreciable change, as judged by refractive index and iodine titer. 2,2-Propanedithiol and phenylmethanedithiol are less stable in storage and suffer 50% decomposition within a month or two under the same conditions.

It would seem that *gem*-dithiols are more stable than *gem*-diols, $R_2C(OH)_2$. Although *gem*-diols are known (*e.g.*, $CCl_3CH(OH)_2$, $C_6H_5COCH(OH)_2$, cyclopropane hydrate) none corresponding to the *gem*-dithiols of the present work have been isolated.

Proof of Structure.—Extensive analytical data (Table II) established the empirical formulas of the *gem*-dithiols. The infrared absorption spectra of 1,1-propanedithiol (Fig. 1) and four other *gem*-dithiols each had a strong absorption maximum at 3.96–3.98 μ, and the Raman spectrum of 1,1-propanedithiol (Fig. 2) had a strong band at 2537 cm.$^{-1}$. These are the locations characteristic of sulfhydryl groups. With 10% aqueous sodium hydroxide solution the compounds either dissolved (with subsequent decomposition) or formed insoluble sodium salts. They were insoluble in 10% aqueous sodium carbonate. All this is strong evidence for the presence of one or more sulfhydryl groups. The compounds reacted readily with iodine to give products best regarded as linear polydisulfides, $-(SCR_2S-)_n$. Titration of the compounds with iodine gave erratic results, but indicated that the number of sulfhydryl groups per molecule is two. Conclusive evidence of this was provided by the acetylation of 1,1-propanedithiol, phenylmethanedithiol and 3,5,5-trimethyl-1,1-hexanedithiol, and by the benzoylation of methanedithiol and phenylmethanedithiol. In all cases two acyl groups per molecule were introduced. The melting points of the two dibenzoates agree with those reported by

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[6] It has been suggested several times that monomeric thials or thiones are responsible for the vile odors that generally accompany the preparation of *s*-trithianes from hydrogen sulfide and aldehydes or ketones in the presence of a strong acid. R. Connor, "Organic Sulfur Compounds," in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 924, gives leading references. The proof of this is not very satisfactory (for example, E. Campaigne, "Thiones and Thials," *Chem. Revs.*, **39**, 4 (1946), says that it is highly questionable whether a monomeric aliphatic thial has ever been prepared), and the possibility that *gem*-dithiols are at least partly responsible seems worth considering. Dr. M. Carmack has suggested to us that the sulfur-containing odor-principle of onions of E. F. Kohman, *Science*, **106**, 625 (1947), may be 1,1-propanedithiol rather than thiopropionaldehyde.

Table II

Properties of *gem*-Dithiols, *gem*-Dithiol Acylates, Polysulfides and Trithianes

Compound	Boiling point °C.	Boiling point Mm.	$n^{25}D$	d^{25}_4 or m.p., °C.	Formula	Analyses, %[a] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found	−SH[q] Calcd.	−SH[q] Found
Methanedithiol	58	89	1.5840		CH_4S_2	15.0	15.4	5.0	5.1	80.0	78.8	82.5	81.1
Methanedithiol dibenzoate[s]				119–119.5	$C_{15}H_{12}O_2S_2$	62.5	62.5	4.2	4.3	22.2	22.2		
1,1-Propanedithiol	60	42[b]	1.5214	1.043	$C_3H_8S_2$	33.3	34.0	7.4	7.5	59.2	59.4	61.1	59.6
1,1-Propanedithiol diacetate	61–62	0.4	1.5150		$C_7H_{12}O_2S_2$	43.7	43.9	6.3	6.6	33.3	34.9		
Phenylmethanedithiol	74–76	0.9	1.6218		$C_7H_8S_2$	53.8	53.9	5.2	5.3	41.0	41.5	42.3	41.6
Phenylmethanedithiol diacetate	122	0.5	1.580[c]	37–38[d]	$C_{11}H_{12}O_2S_2$	55.0	55.1	5.0	5.2	26.7	27.0		
Phenylmethanedithiol dibenzoate[p]				137–138	$C_{21}H_{16}O_2S_2$	69.2	69.3	4.4	5.0	17.6	17.6		
3,5,5-Trimethyl-1,1-hexanedithiol	60–63	0.5	1.4875	0.935	$C_9H_{20}S_2$[e]	56.2	57.6	10.5	10.8	33.3	32.4	34.4	32.6
3,5,5-Trimethyl-1,1-hexanedithiol diacetate	96–100	0.2	1.4930		$C_{13}H_{24}O_2S_2$	56.5	57.3	8.7	8.9	23.2	23.0		
2,2-Propanedithiol	61–62	105[f]	1.5063	1.006[r]	$C_3H_8S_2$	33.3	33.9	7.4	7.9	59.2	58.6	61.1	73.0
3,3-Pentanedithiol	80–82	47	1.5042		$C_5H_{12}S_2$	44.1	45.9	8.9	9.1	47.1	44.9	48.5	64.7
1,1-Cyclohexanedithiol	69–73	6	1.5440	1.083	$C_6H_{12}S_2$[g]	48.6	49.4	8.2	8.6	43.2	43.4	44.6	50.0
Propyl disulfide[h]	194	760	1.4961										
Propyl trisulfide	68–69	0.9	1.5424		$C_6H_{14}S_3$	39.5	41.4	7.7	8.0	52.7	51.1		
Isopropyl disulfide[h,i]	97–98	71[j]	1.4891		$C_6H_{14}S_2$	47.9	48.4	9.4	9.6	42.7	43.3		
Isopropyl trisulfide	75–76	5	1.5351		$C_6H_{14}S_3$	39.5	40.5	7.7	7.9	52.7	53.1		
Isopropyl tetrasulfide	88	0.5	1.5812		$C_6H_{14}S_4$	33.6	34.1	6.6	6.1	59.8	60.3		
Benzyl disulfide[k]				66.5–68[l]									
Cyclohexyl disulfide[m]	110	0.7	1.5462		$C_{12}H_{22}S_2$	62.5	62.7	9.6	10.1			230[n]	210[n]
3,5,5-Trimethylhexyl disulfide	128–129	0.4	1.4803	0.901	$C_{18}H_{38}S_2$	67.9	68.1	12.0	12.2	20.1	21.6		
$CH_3CHCH_2CH_2CH(CH_3)SS$	66–69	10	1.5461		$C_6H_{12}S_2$	48.7	50.6	8.1	7.7	43.2	43.4		
$CH_3CHCH_2CH_2CH(CH_3)SSS$ [t]	54	0.5	1.5639		$C_6H_{12}S_3$	40.0	42.4	6.7	6.9	53.3	52.0		
α-2,4,6-Triphenyltrithiane[o]				164–166[l]	$C_{21}H_{18}S_3$	68.8	69.0	5.0	5.1				
β-2,4,6-Triphenyltrithiane[o]				227–228[l]	$C_{21}H_{18}S_3$	68.8	69.1	5.0	5.1				

[a] Average of two determinations differing by less than 0.4%. [b] B.p. 142° (760 mm.). [c] Supercooled liquid. [d] Recrystallized from pentane. [e] Mol. wt.: calcd. 192; found (cryoscopic in benzene), 212. [f] B.p. 113–116° (760 mm.). [g] Mol. wt.: calcd. 148; found (cryoscopic in benzene), 170. [h] A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, 16 (1943); D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler, This Journal, **73**, 3627 (1951). [i] Infrared spectrum identical with that of an authentic sample. [j] B.p. 176° (760 mm.). [k] I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, 483 (1946). [l] M.p. not depressed by mixing with authentic sample. [m] G. F. Bloomfield, *J. Soc. Chem. Ind.* (*London*), **67**, 14 (1948); B. Weibull, *Arkiv Kemi., Mineral. Geol.*, **23A**, No. 18 (1946). [n] Mol. wt., ebullioscopic in benzene. [o] J. F. Suyver, *Rec. trav. chim.*, 24, 397 (1905). [p] H. Behringer, *Ann.*, **564**, 219 (1949), reports m.p. 139–140.5°. [q] Determined iodimetrically. [r] M.p. 4–8°. [s] H. L. Wheeler and H. F. Merriam, This Journal, **24**, 444 (1902), report m.p. 120°. [t] Despite the seven-membered ring, an unbranched sulfur chain is favored in view of such papers as H. P. Koch, *J. Chem. Soc.*, 394 (1949), and O. Foss, *Acta Chem. Scand.*, 4, 404 (1950).

other workers, who used different methods of synthesis.

$$RCH(SH)_2 + 2(CH_3CO)_2O \longrightarrow RCH(SCOCH_3)_2 + 2CH_3COOH$$

That at least one of the sulfhydryl groups is on the carbon atom originally bearing oxygen was shown by reducing four of the compounds with lithium aluminum hydride. A mercaptan and hydrogen sulfide were formed in good yield in accordance with the equation

$$R_2C(SH)_2 \xrightarrow{LiAlH_4} R_2CHSH + H_2S$$

That the two sulfhydryl groups are on the same carbon atom was shown by heating 2,2-propanedithiol with hydrochloric acid and 2,4-dinitrophenylhydrazine in ethanol. Acetone 2,4-dinitrophenylhydrazone was obtained in 37% yield.

$$Me_2C(SH)_2 \xrightarrow[2,4\text{-DNPH}]{H_3O^+} Me_2C{=}NNHC_6H_3(NO_2)_2$$

1,1-Propanedithiol gave no hydrazone under the same conditions. However, after preliminary treatment of the dithiol with hot alcoholic lead acetate, propionaldehyde 2,4-dinitrophenylhydrazone was obtained in 41% yield. The lead acetate precipitated an unstable lead derivative that immediately decomposed with formation of lead sulfide. It seems likely that thiopropionaldehyde was formed simultaneously and that it was this that reacted with 2,4-dinitrophenylhydrazine.

$$EtCH(SH)_2 + Pb^{++} \longrightarrow \text{—}(\text{-}SCHEtSPb\text{-})_n\text{—} \xrightarrow{\text{heat}}$$

$$PbS + EtCHS \xrightarrow[2,4\text{-DNPH}]{H_3O^+} EtCH{=}NNHC_6H_3(NO_2)_2$$

Conclusive proof of the structure of the *gem*-dithiols was provided by alkylation experiments with olefins in the presence of free radicals. 3,5,5-Trimethyl-1,1-hexanedithiol reacted with ethylene or propylene, 1,1-propanedithiol with ethylene, and 2,2-propanedithiol with propylene to give the dialkylated derivatives, $R_2C(SR')_2$, in 7–32% yield. The structures of the products of the last two alkylations were proved by comparing their physical properties, including infrared spectra (Fig. 1), with those of authentic samples prepared as shown in the equations

$$EtCH(SH)_2 \xrightarrow{C_2H_4} EtCH(SEt)_2 \xleftarrow[BF_3]{EtSH} EtCHO$$

$$Me_2C(SH)_2 \xrightarrow{C_3H_6} Me_2C(SPr)_2 \xleftarrow[BF_3]{n\text{-}PrSH} Me_2CO$$

Chemical Properties of *gem*-Dithiols.—Several chemical properties less pertinent to the structure-proof of the *gem*-dithiols than those discussed above were determined. When 3,5,5-trimethyl-1,1-hexanedithiol was heated to 220°, 0.86 mole of hydrogen sulfide per mole of dithiol was liberated. The chief other product was 3,5,5-trimethylhexyl disulfide (58% yield). Sulfur and material believed to contain 3,5,5-trimethylhexyl trisulfide were also

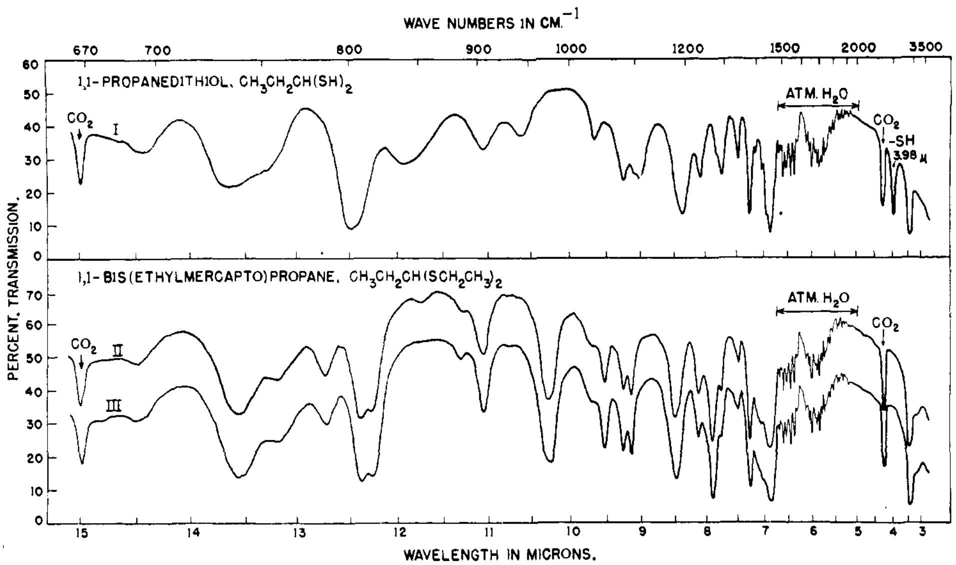


Fig. 1.—Infrared absorption spectra of: I, 1,1-propanedithiol; II, 1,1-bis-(ethylmercapto)-propane from 1,1-propanedithiol and ethylene (curve displaced upward); and III, 1,1-bis-(ethylmercapto)-propane from propionaldehyde and ethyl mercaptan.

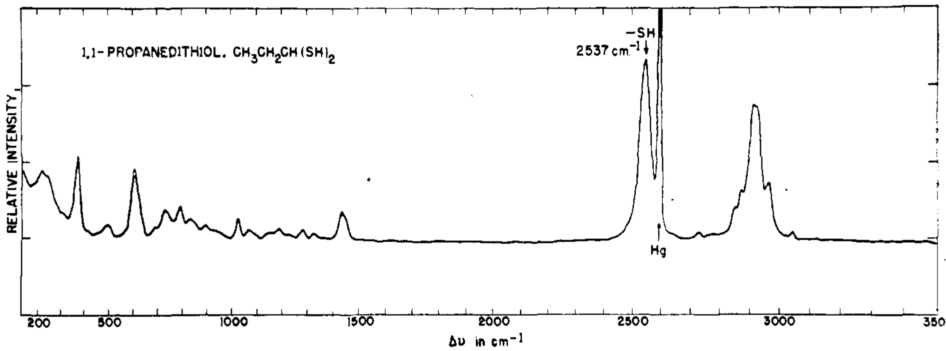
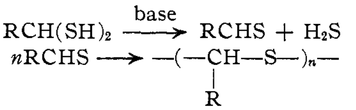


Fig. 2.—Raman spectrum of 1,1-propanedithiol.

formed. This pyrolysis seems best described by the equations below. The excess of hydrogen sulfide over that called for by the equations may have been caused by sulfur abstracting hydrogen from the various substances present.

$$2C_8H_{17}CH(SH)_2 \xrightarrow{\text{heat}} (C_8H_{17}CH_2)_2S_2 + H_2S + S$$
$$(C_8H_{17}CH_2)_2S_2 + S \longrightarrow (C_8H_{17}CH_2)_2S_3$$

The addition of potassium hydroxide, even a trace, to ice-cold methanol solutions of 3,5,5-trimethyl-1,1-hexanedithiol caused decomposition of the dithiol. One of the reaction products was hydrogen sulfide, 0.73 and 1.13 moles per mole of dithiol being formed under different conditions. The second important product was a low-melting solid whose composition suggested that it was a linear polymer of 3,5,5-trimethylhexanethial. Treatment of 1,1-propanedithiol with sodium hydroxide or pyridine in the presence of 2,4-dinitrochlorobenzene gave 38–45% yields of bis-(2,4-dinitrophenyl) sulfide instead of the desired $EtCH(SC_6H_3N_2O_4)_2$. These results can be accounted for by the equations



$$RCH(SH)_2 \xrightarrow{\text{base}} RCHS + H_2S$$
$$n\text{RCHS} \longrightarrow \text{—(—}\underset{\displaystyle R}{\underset{|}{CH}}\text{—S—)}_n\text{—}$$

Solutions of mercuric cyanide, copper sulfate, silver nitrate or lead acetate react with *gem*-dithiols to give precipitates ranging in color from white to orange. These precipitates break down spontaneously or on gentle heating to give dark-colored metal sulfides. An alcoholic solution of lead acetate is a sensitive reagent for detecting *gem*-dithiols. An orange precipitate that soon turns black readily distinguishes between a *gem*-dithiol and either a mercaptan, which gives a stable yellow precipitate, or hydrogen sulfide, which of course gives an immediate black precipitate.

Strong acids, in contrast to bases, have little effect on *gem*-dithiols. Thus, 3,5,5-trimethyl-1,1-hexanedithiol was recovered unchanged after standing in contact with boron fluoride etherate for 48 hours.

A mixture of a *gem*-dithiol with an aldehyde, but not with a ketone, gradually becomes more viscous and increases in refractive index on standing several hours. During this time a strong O–H band gradually appears in the infrared absorption spectrum of the mixture and the bands due to –CHO and S–H greatly diminish in intensity. The starting materials can be recovered by distillation of the mixture. The following equations explain these facts.

$$R_2C(SH)_2 + R'CHO \rightleftarrows R_2C(SH)SCH(OH)R'$$

$$R'CHO + R_2C(SH)SCH(OH)R' \rightleftarrows R'CH(OH)SCR_2SCH(OH)R'$$

Addition of boron fluoride to such mixtures causes rapid elimination of water with formation of complex mixtures of unidentified, distillable products.

An attempt to convert 3,5,5-trimethyl-1,1-hexanedithiol to a disulfonic acid by oxidation with nitric acid gave instead 3,5,5-trimethylhexanoic acid mixed with another acid, probably 2,4,4-trimethylpentanoic acid.

$$C_8H_{17}CH(SH)_2 \xrightarrow{HNO_3} C_8H_{17}COOH + C_7H_{15}COOH + H_2SO_4$$

Polysulfides.—There is at least one known case in which a ketone (acetophenone) is converted to a disulfide by treatment with hydrogen sulfide and ammonia.[7] However, the formation of polysulfides by merely heating aldehydes or ketones with hydrogen sulfide under pressure is a reaction apparently not previously observed. Yields of polysulfide mixtures as high as 60% were encountered in the present work and higher yields are probably possible. The polysulfide mixtures were generally separated into their components by fractional distillation, although sometimes the products were so similar in boiling point that this was difficult.

Benzyl disulfide was identified by the mixed melting point method, isopropyl disulfide by comparison of its infrared absorption spectrum with that of an authentic sample, and propyl disulfide and cyclohexyl disulfide by comparison of physical properties with those reported in the literature. Identification of the others was chiefly on the basis of elemental analyses. The structures of isopropyl trisulfide, isopropyl tetrasulfide and propyl trisulfide were confirmed by reducing them to the corresponding mercaptans with lithium aluminum hydride. Others have reduced disulfides[8,9] and a trisulfide[8] to mercaptans by this means

As has been mentioned above, pyrolysis of a *gem*-dithiol results in polysulfide formation. It was noted in several pairs of experiments identical except for reaction temperature that a lower yield of *gem*-dithiol and a higher yield of polysulfide were obtained at the higher temperature. This suggests that *gem*-dithiols may be precursors of the polysulfides isolated by us.

Experimental

Reactions of Aldehydes and Ketones with Hydrogen Sulfide.—Three methods were used. One example of each is given below. These examples also illustrate how the *gem*-dithiols and polysulfides were separated and purified; in general this involved distillation. Over ninety runs were made in the course of this study. Conditions and products of twenty of these runs are shown in Table I. The physical properties and analytical data of the *gem*-dithiols and other products are listed in Table II.

Method A.—3,5,5-Trimethylhexanal (895 g., Rohm and Haas Co.) was placed in a 12-l. stainless-steel autoclave equipped with a stirrer. The autoclave was cooled to −30°, its internal pressure was lowered to 20 mm., and 3700 g. of hydrogen sulfide was distilled into it. The mixture was heated to 50° with stirring, stirred at this temperature for 15 hours, and cooled to 25°. Hydrogen sulfide was bled off, the reaction mixture was mixed with one liter of ether, and the ether layer was washed with water, dried over magnesium sulfate, and freed of ether at 25° (20 mm.). The residue (1045 g.) was distilled through a 15-cm. indented Claisen still-head in two equal batches.[10] The following fractions were obtained: A, 3,5,5-trimethylhexanal, 59 g., pot temp. 50–69°, b.p. 25–50° (0.5 mm.), $n^{25}D$ 1.427; B, 3,5,5-trimethylhexanal containing about 20% of 3,5,5-trimethyl-1,1-hexanedithiol, 196 g., pot temp. 69–78°, b.p. 50–59° (0.5 mm.), $n^{25}D$ 1.436; C, 3,5,5-trimethyl-1,1-hexanedithiol containing 15–20% of 3,5,5-trimethylhexanal, 339 g., pot temp. 78–152°, b.p. 58° (0.6 mm.) to 78° (1.5 mm.), $n^{25}D$ 1.485; D, pot residue, 387 g. The amount of *gem*-dithiol in fractions A-C was best estimated by sulfur analysis, neither titration with iodine nor measurement of refractive index being reliable for this purpose. It was estimated that fractions A-C contained 275 g. (31% recovery) of 3,5,5-trimethylhexanal and 319 g. (26% yield) of 3,5,5-trimethyl 1,1-hexanedithiol.

3,5,5-Trimethyl-1,1-hexanedithiol underwent extensive decomposition on attempted vacuum-distillation through an efficient packed column. Accordingly it was necessary to redistil fractions A-C separately through the Claisen still-head, combine like fractions, and redistil these. By this laborious means a total of about 200 g. (17% yield) of *gem*-dithiol of 95% purity was obtained. A portion of this was redistilled and a middle fraction was used for analytical purposes.

Fraction D, the pot residue, was oxygen-free. It contained about 38% of *gem*-dithiol as shown by infrared analysis and titration with iodine. The *gem*-dithiol could not be removed by distillation because at pot temperatures above about 150° it decomposed with evolution of hydrogen sulfide so rapidly that a good enough vacuum could not be maintained. The remainder of D was probably a mixture of 3,5,5-trimethylhexyl disulfide and trisulfide, as the following experiment indicated. The residue was heated at 225° under nitrogen for one hour to decompose the *gem*-dithiol and was then distilled. Besides 27 g. of forerun and 46 g. of residue, 286 g. of material of b.p. 120–147° (1.0 mm.) and $n^{25}D$ 1.483–1.501 was obtained. Its sulfur content (22.3%) indicated that it was about 70% disulfide and 30% trisulfide. It was possible to separate 65 g. of high-quality 3,5,5-trimethylhexyl disulfide by redistillation of this material.

Method B.—A mixture of 160 g. of cyclohexanone and 190 g. of hydrogen sulfide was placed in a 400-ml. silver-lined shaker-tube. The mixture was agitated at 30° while 115 g. of cyclohexanone was gradually injected into the tube at a rate that maintained a pressure of 700–1000 atm. throughout the reaction. After 15 hours the agitation was stopped, the hydrogen sulfide was bled off, and the reaction mixture was worked up as described under method A. The following fractions were obtained on distillation:

Fract.	Wt., g.	B.p. °C. (6 mm.)	$n^{25}D$	Approx. % dithiol
A	74	33–50	1.458	9
B	50	50–59	1.482	40
C	53	59–66	1.522	77
D	89	66	1.544	100
E	3	(Residue)		

The amount of *gem*-dithiol in each fraction could be estimated from its refractive index or by titration with iodine. Such estimates indicated that fractions A–D contained 109 g. (40% recovery) of cyclohexanone and 157 g. (38% yield) of 1,1-cyclohexanedithiol. Fractions B and C were combined and redistilled. A dithiol-rich fraction was combined with D, and this on redistillation gave 75 g. (18% yield) of high-quality 1,1-cyclohexanedithiol, b.p. 69–73° (6 mm.), $n^{25}D$ 1.5440, besides fractions of lesser purity.

Method C.—A mixture of 3.11 g. of acetone, 3.31 g. of hydrogen sulfide and 0.11 g. of nitrogen was placed in a stainless-steel cylinder with a moveable piston. The cylinder was placed in a Bridgman-type pressure apparatus[11] and its contents were subjected to a pressure of 7000–8500

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(7) E. Baumann and E. Fromm, *Ber.*, **28**, 907 (1895).

(8) R. C. Arnold, A. P. Lien and R. M. Alm, This Journal, **72**, 731 (1950).

(9) J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 638 (1950).

(10) With batches of much over 600 g., there was extensive decomposition of the *gem*-dithiol during distillation.

(11) P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, London, 1949, pp. 30–59.

atm. at 30° for 15 hours. The reaction mixture was taken up in ether and the ether extract was combined with the extract from a duplicate run. The combined extracts were washed with water, dried over magnesium sulfate, and distilled through a 15-cm. indented Claisen still-head. Crude 2,2-propanedithiol (3.05 g., 26% yield) was collected at 40–54° (70 mm.). A second fraction, 0.42 g., b.p. 46–74° (23 mm.), was crude isopropyl disulfide (5% yield). The residue in the distillation pot amounted to only 0.05 g. The 2,2-propanedithiol fraction was redistilled through a 13 × 0.6 cm. vacuum-jacketed glass tube containing a glass spiral. A middle fraction, b.p. 61–62° (105 mm.), $n^{25}\text{D}$ 1.5063, was taken for analysis.

The above experiment was repeated at 80°. The first distillation gave as principal fractions the following: A, crude isopropyl disulfide, 4.02 g. (50% yield), b.p. 68–71° (21 mm.), $n^{29}\text{D}$ 1.4882; B, a middle fraction probably containing isopropyl trisulfide, 0.89 g., b.p. 33–62° (1 mm.); C, crude isopropyl tetrasulfide, 1.25 g. (11% yield), b.p. 68–87° (1 mm.), $n^{30}\text{D}$ 1.5972; and D, 1.81 g. of viscous residue. Fractions B and D were discarded. Fractions A and C were redistilled and identified by analysis of middle fractions.

Infrared and Raman Spectra.—Infrared spectra were obtained with a Perkin–Elmer infrared spectrometer model 12B having a rock salt prism. The sample cell was approximately 0.0015 inch thick. 1,1-Propanedithiol (Fig. 1), 2,2-propanedithiol, 3,3-pentanedithiol, 1,1-cyclohexanedithiol and 3,5,5-trimethyl-1,1-hexanedithiol each had a strong absorption maximum, believed to be due to S–H, in the 3.96–3.98 μ region. The spectrum of 1-hexanethiol was determined for comparison. Its corresponding maximum was at a slightly shorter wave length (3.95 μ) and was much weaker, being only about one-tenth as strong as that of 1,1-cyclohexanedithiol.

The Raman spectrum of 1,1-propanedithiol (Fig. 2) was determined with an instrument similar to one described elsewhere.[12] There was a strong Raman line, probably due to S–H, at 2537 cm.$^{-1}$. This is a slightly lower frequency than the S–H Raman line of ordinary mercaptans (2567–2579 cm.$^{-1}$).[13]

Oxidation of 3,5,5-Trimethyl-1,1-hexanedithiol by Iodine.—A solution of 6.6 g. (26 mmoles) of iodine in 75 ml. of ether was added dropwise to a mixture of 100 ml. of water and 200 ml. of ether containing 5.0 g. (26 mmoles) of the dithiol. The mixture was stirred at 0–5° during the addition and for one hour longer. The excess iodine was reduced with sodium bisulfite and the ether layer was separated, washed with water, and dried. Removal of the ether left 5.1 g. of a viscous, pale-yellow oil soluble in hexane or benzene but insoluble in alcohol. It had approximately the composition of a polydisulfide of low molecular weight.

Anal. Calcd. for $(C_9H_{18}S_2)_{2.4}$: C, 56.8; H, 9.5; S, 33.7; mol. wt., 455. Found: C, 57.6; H, 9.65; S, 31.4; mol. wt. (ebullioscopic in benzene), 455.

Other *gem*-dithiols gave similar polymers which, however, were not analyzed.

A similar experiment in which hydrogen peroxide was added to an acetic acid solution of 3,5,5-trimethyl-1,1-hexanedithiol gave an oil similar in appearance and composition to that above. In a control experiment, the dithiol was recovered unchanged after standing several days dissolved in acetic acid containing no hydrogen peroxide.

Acetylation of *gem*-Dithiols.—3,5,5-Trimethyl-1,1-hexanedithiol (58.6 g.) was added to 75.6 g. (15% excess) of acetic anhydride in 117 g. of pyridine at 25°. After 18 hours at 25°, the mixture was distilled. The diacetate (59.1 g., 71% yield) was collected at 96–116° (0.4 mm.). It was redistilled and a middle portion, b.p. 96–100° (0.2 mm.), $n^{25}\text{D}$ 1.4930, was analyzed.

1,1-Propanedithiol diacetate, phenylmethanedithiol diacetate, methanedithiol dibenzoate and phenylmethane dithiol dibenzoate were prepared similarly. In each of the latter two cases, benzoyl chloride replaced acetic anhydride, the reaction mixture was poured into ice-water, and the solid which precipitated was recrystallized from ethanol.

An attempt was made to prepare 1,1-propanedithiol diacetate by condensing propionaldehyde with thiolacetic acid in the presence of boron fluoride etherate under conditions described below for the preparation of 1,1-bis-(ethylmercapto)-propane. However, the product was a complex mixture boiling higher than 1,1-propanedithiol diacetate.[14]

The properties and analytical data of the four *gem*-dithiol diacylates are listed in Table II.

Reduction of *gem*-Dithiols and Polysulfides with Lithium Aluminum Hydride.—Anhydrous ether (20 ml.) was added to 0.27 g. (6.4 mmoles) of 90% lithium aluminum hydride. The ether was refluxed for one hour and 0.60 g. (5.6 mmoles) of 2,2-propanedithiol was then added dropwise at a rate which maintained steady refluxing. The mixture was refluxed 30 minutes, cooled in ice, and added dropwise with swirling to a mixture of 5.5 ml. of 6 *N* sulfuric acid and 30 g. of ice. The ether layer was separated, washed with water, and added to a mixture of 2.2 ml. (5.6 mmoles) of 2.5 *N* sodium hydroxide and 25 ml. of absolute ethanol. To this 1.13 g. (5.6 mmoles) of 2,4-dinitrochlorobenzene was added. The resultant mixture was concentrated to a volume of about 6 ml. on a steam-bath and filtered while hot. The cooled filtrate deposited 0.63 g. (47% yield) of isopropyl 2,4-dinitrophenyl sulfide, m.p. 89–91°. After recrystallization from ethanol it melted at 91–92° alone or mixed with an authentic sample.

The following substances were treated similarly (the m.p. and yield of each alkyl 2,4-dinitrophenyl sulfide are given in parentheses): 1,1-propanedithiol (84–85°, 52%); 3,3-pentanedithiol (52–53°, 48%); 1,1-cyclohexanedithiol (146–147°, 55%); isopropyl trisulfide (90–91.5°, 65%); isopropyl tetrasulfide (88.5–90°, 12%); propyl trisulfide (82–83.5°, 66%). The reported melting points of *n*-propyl, isopropyl and cyclohexyl 2,4-dinitrophenyl sulfide are 81°,[15] 94.5°[15] and 148°,[16] respectively. Mixed melting point determinations with authentic samples verified the identities of the first two. 3-Pentyl 2,4-dinitrophenyl sulfide has not been previously reported.

Anal. Calcd. for $C_{11}H_{14}N_2O_4S$: C, 48.9; H, 5.2. Found: C, 49.4; H, 5.3.

3-Pentyl 2,4-dinitrophenyl sulfone, prepared by oxidation of the sulfide with hydrogen peroxide in acetic acid, melted at 139–140° after three recrystallizations from ethanol.

Anal. Calcd. for $C_{11}H_{14}N_2O_6S$: C, 43.7; H, 4.7; N, 9.3. Found: C, 44.3; H, 5.1; N, 9.9.

The gases evolved on decomposition of the reaction mixture from 1,1-propanedithiol were passed through aqueous copper sulfate, causing copper sulfide to precipitate in 58% yield.

Acetone 2,4-Dinitrophenylhydrazone from 2,2-Propanedithiol.—A solution of 0.54 g. of 2,2-propanedithiol, 0.99 g. of 2,4-dinitrophenylhydrazine and 7.5 ml. of 12 *N* hydrochloric acid in 75 ml. of 95% ethanol was boiled for 5 hours. The cooled solution deposited 0.44 g. (37% yield) of acetone 2,4-dinitrophenylhydrazone. Its melting point after recrystallization from ethanol was 123–124° alone or mixed with an authentic sample.

Propionaldehyde 2,4-Dinitrophenylhydrazone from 1,1-Propanedithiol.—The above procedure gave no hydrazone with 1,1-propanedithiol although propionaldehyde gave propionaldehyde 2,4-dinitrophenylhydrazone in 61% yield. Lead acetate trihydrate (7.58 g., 20 mmoles) was dissolved in 20 ml. of water. The solution was diluted with 150 ml. of 95% ethanol, 1.98 g. (10 mmoles) of 2,4-dinitrophenylhydrazine was added, and the mixture was boiled to dissolve the hydrazine. Addition to the hot solution of 1.08 g. (10 mmoles) of 1,1-propanedithiol dissolved in 20 ml. of ethanol caused an immediate heavy precipitate of lead sulfide. Ten milliliters of 12 *N* hydrochloric acid was added. The mixture was boiled 5 minutes and filtered while hot. The filtrate deposited 1.25 g. of a mixture of lead chloride and propionaldehyde 2,4-dinitrophenylhydr-

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[12] M. R. Fenske, W. G. Braun, R. V. Wiegand, D. Quiggle, R. H. McCormick and D. H. Rank, *Anal. Chem.*, **19**, 700 (1947).

[13] J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, N. Y., 1939, p. 257.

[14] J. Bongartz, *Ber.*, **19**, 1934 (1886), treated benzaldehyde with thiolacetic acid under similar conditions and obtained in 10% yield a substance of m.p. 147–148° which he believed to be phenylmethanedithiol diacetate. This melting point is much higher than the value 37–38° observed for phenylmethanedithiol diacetate in this work. Bongartz did not establish his structure by analysis or other means so that there is reason to question the identity of his compound.

[15] R. W. Bost, J. O. Turner and R. D. Norton, THIS JOURNAL, **54**, 1985 (1932).

[16] R. W. Bost, J. O. Turner and M. W. Conn, *ibid.*, **55**, 4957 (1933).

zone from which the latter (0.98 g., 41% yield; m.p. 150–152°) was separated by extraction with boiling ethanol. A mixture with an authentic sample (m.p. 152–153°) melted at 151–153°.

1,1-Bis-(ethylmercapto)-propane.—A mixture of 4.10 g. of 1,1-propanedithiol, 2.82 g. (33% excess) of ethylene and 0.15 g. of α,α'-azodiisobutyronitrile was heated at 80° and 8000 atm. for 13 hours. Distillation gave 2.95 g. of a complex mixture, b.p. 35–136° (9 mm.), n^{14}D 1.477–1.546. Crude 1,1-bis-(ethylmercapto)-propane (0.93 g., 15% yield) was collected at 75–77° (9 mm.) during this distillation. An analytical sample, b.p. 73–76° (8 mm.), n^{25}D 1.4971, was obtained by redistillation of this fraction.

Anal. Calcd. for $C_7H_{16}S_2$: C, 51.2; H, 9.8. Found; C, 51.75; H, 9.8.

A mixture of 15.0 g. of propionaldehyde, 35.0 g. (10% excess) of ethyl mercaptan, and 3.0 ml. of boron fluoride etherate at 25° for 24 hours gave 35.6 g. (84% yield) of 1,1-bis-(ethylmercapto)-propane, b.p. 70–75° (7 mm.), n^{25}D 1.4969, d^{25}_4 0.954. Its infrared absorption spectrum (Fig. 1) was identical with that of 1,1-bis-(ethylmercapto)-propane obtained from 1,1-propanedithiol and ethylene.

Anal. Found: C, 51.75; H, 10.0.

2,2-Bis-(propylmercapto)-propane.—2,2-Bis-(propylmercapto)-propane was prepared from 2,2-propanedithiol and propylene under the conditions described for 1,1-bis-(ethylmercapto)-propane. The yield of once-distilled product was 32%. The analytical sample had the following properties: b.p. 81–82° (5 mm.), 234–235° (760 mm.); n^{25}D 1.4905.

Anal. Calcd. for $C_9H_{20}S_2$: C, 56.2; H, 10.5; S, 33.3. Found: C, 56.5; H, 10.5; S, 34.3.

Condensation of acetone with propyl mercaptan by the method of the preceding section gave a 55% yield of 2,2-bis-(propylmercapto)-propane; b.p. 81° (5 mm.); n^{25}D 1.4888. The infrared absorption spectra of the two samples of 2,2-bis-(propylmercapto)-propane were identical.

Anal. Found: C, 56.6; H, 10.6.

1,1-Bis-(ethylmercapto)- and 1,1-Bis-(propylmercapto)-3,5,5-trimethylhexane.—A mixture of 50.0 g. of 3,5,5-trimethylhexanedithiol, 101 g. of propylene and 1.0 g. of α,α'-azodiisobutyronitrile was placed in a 400-ml. silver-lined tube. The agitated mixture was heated to 75°, pressured to 1000 atm. with propylene, and held at 900–1000 atm. and 75° for 15 hours. Distillation in a Vigreux column gave 36.4 g. of a complex oil, b.p. 30–174° (0.9 mm.), and 1.6 g. of residue. Redistillation of a 14.6-g. fraction of b.p. 80–123° (0.9 mm.) gave 6.9 g. (10% yield) of crude 1,1-bis-propylmercapto)-3,5,5-trimethylhexane, b.p. 97–109° (1.1 mm.). Two redistillations gave a fraction suitable for analysis; b.p. 99–100° (0.9 mm.); n^{25}D 1.4849.

Anal. Calcd. for $C_{15}H_{32}S_2$: C, 65.1; H, 11.7; S, 23.2. Found: C, 65.0; H, 11.8; S, 24.9.

Under similar conditions, 3,5,5-trimethyl-1,1-hexanedithiol and ethylene gave crude 1,1-bis-(ethylmercapto)-3,5,5-trimethylhexane in 7% yield. Material of b.p. 79–80° (0.6 mm.) and n^{25}D 1.4850 was obtained on redistillation.

Anal. Calcd. for $C_{13}H_{28}S_2$: C, 62.8; H, 11.4; S, 25.8. Found: C, 62.9; H, 11.5; S, 26.6.

Pyrolysis of 3,5,5-Trimethyl-1,1-hexanedithiol.—A slow stream of nitrogen was bubbled through 15.6 g. of 3,5,5-trimethyl-1,1-hexanedithiol in a 25-ml. flask equipped with a thermometer and condenser. The off-gas passed through 200 ml. of 6% sodium hydroxide. The dithiol was heated to 160° in about 5 minutes and to 220° during the next 45 minutes. Heating was stopped but passage of nitrogen continued for 65 hours. Titration of the sodium hydroxide solution with iodine indicated that 0.86 mole of hydrogen sulfide per mole of dithiol had been liberated. Distillation of the flask-contents gave, besides 2.4 g. of forerun and 0.3 g. of residue, two fractions: A, 7.5 g., b.p. 129–146° (0.8 mm.), and B, 3.8 g., b.p. 165–185° (1.0 mm.). Redistillation of A showed that it was mainly 3,5,5-trimethylhexyl disulfide (58% yield). Fraction B on standing several days deposited 0.07 g. of sulfur. The liquid remaining had a refractive index of 1.5131^{25}D; it was probably mostly 3,5,5-trimethylhexyl trisulfide, although its identity was not definitely established.

Test-tube experiments showed that decomposition began at about 150° and was rapid at 200°. The presence of ethylenediamine (5% by weight) caused decomposition to begin at 65°. Similar amounts of acetic acid or 85% phosphoric acid had little effect on the temperature at which decomposition of the dithiol began.

The Decomposition of 3,5,5-Trimethyl-1,1-hexanedithiol by Bases. (a).—A solution of 5.00 g. (26 mmoles) of the dithiol in 50 ml. of methanol was stirred at 0–5° under a stream of nitrogen while a solution of 3.4 g. (52 mmoles) of 85% potassium hydroxide in a mixture of 5 ml. of water and 25 ml. of methanol was added dropwise in a period of 15 minutes. Stirring was continued at 0–5° for 3 hours and at 25° for 15 hours. A thick oil which slowly solidified gradually precipitated. The solid was suspended in methanol and pulverized in a Waring Blendor to give 1.86 g. of white powder, m.p. 52–58°, that at 25° was almost insoluble in methanol or acetic acid, moderately soluble in acetone, and very soluble in hexane, butanol or most other organic solvents.

Anal. Calcd. for $(C_9H_{18}S)_{24}$: C, 68.3; H, 11.5; S, 20.25; mol. wt., 3800. Found: C, 66.6; H, 11.25; S, 20.5; mol. wt. (ebullioscopic in benzene), 3700, 4000.

(b).—Experiment (a) was repeated using only 0.10 g. (1.5 mmoles) of potassium hydroxide. The off-gas passed through 3% sodium hydroxide solution. The sulfur content of the latter (measured as barium sulfate) corresponded to 0.73 mole of hydrogen sulfide having been evolved per mole of dithiol. In the absence of potassium hydroxide no hydrogen sulfide was evolved and 3,5,5-trimethylhexanedithiol was recovered unchanged.

(c).—Experiment (a) was repeated except that as soon as all the base had been added, the cold solution was acidified with dilute methanolic sulfuric acid. The acidification caused immediate liberation of 1.13 moles of hydrogen sulfide per mole of dithiol.

(d).—After 24 hours at 25°, a solution of 5.0 g. of the dithiol in 10.0 g. of pyridine was taken up in ether and washed with 2 *N* hydrochloric acid. Subsequent distillation at 0.3 mm. separated 2.2 g. of the dithiol from 2.3 g. of decomposition product not volatile at 160°.

The Decomposition of 1,1-Propanedithiol by Bases.—A solution of 1.00 g. (9.2 mmoles) of 1,1-propanedithiol and 3.75 g. (18.4 mmoles) of 2,4-dinitrochlorobenzene in 40 ml. of ethanol was treated with 7.4 ml. (18.4 mmoles) of 2.5 *N* sodium hydroxide. The mixture was boiled five minutes and filtered while hot. The filtrate deposited crude bis-(2,4-dinitrophenyl) sulfide that, after recrystallization from acetic acid, weighed 1.28 g. (38% yield) and melted at 192–194° alone or mixed with an authentic sample.[17]

Replacement of the sodium hydroxide by an equivalent amount of pyridine (1.46 g.) gave similar results, the yield of bis-(2,4-dinitrophenyl) sulfide being 1.53 g. (45%).

The Lead Acetate Test for *gem*-Dithiols.—The reagent is prepared by dissolving 5.0 g. of lead acetate trihydrate in 10 ml. of hot water containing 0.2 ml. of acetic acid, and diluting the solution to 100 ml. with absolute ethanol. Addition of a drop of *gem*-dithiol to 0.5 ml. of reagent at 25° gives an orange precipitate which generally turns black in anywhere from 30 seconds to 10 minutes, depending on the dithiol. In the rare instances when the precipitate has not turned black after 10 minutes, placing the test-tube in a bath at 60° generally causes blackening within two minutes. In contrast, mercaptans (*e.g.*, 1-butanethiol, thiophenol) give yellow precipitates which do not darken even on standing at 60° for 20 minutes. If hydrogen sulfide, which gives an immediate black precipitate, is present, it must be removed before testing; a good way is to codistil it with ether at reduced pressure and 25°. The test has been successfully applied to organic mixtures containing less than 1% *gem*-dithiol.

The Reactions of *gem*-Dithiols with Aldehydes and Ketones. (a).—The refractive index (n^{25}D) of a mixture of 1.84 g. of 3,5,5-trimethylhexanal and 2.72 g. of 3,5,5-trimethyl-1,1-hexanedithiol was determined at 20-minute intervals. It rose steadily from 1.458 to 1.477 in about 3.5 hours and then remained constant. Several infrared absorption spectra were determined during the same period. An O–H band, initially absent, became visible at 3.0 μ after 30 minutes and was strong after 3.5 hours. The initially-strong aldehyde C–H band at 3.7 μ was only one-fifth as strong after 3.5 hours. In the same period of time the in-

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(17) F. Beilstein and A. Kurbatow, *Ann.*, **197**, 75 (1879).

tensity of the S–H band at 3.97 μ was reduced by half and that of the C=O band at 5.8 μ was also considerably reduced. There was no further spectral change in 5 days. A mixture that had stood several hours at 25° was more viscous than a fresh mixture.

Similar behavior was observed when 1-butanethiol or 1,1-cyclohexanedithiol was mixed with 3,5,5-trimethylhexanal or when 3,5,5-trimethyl-1,1-hexanedithiol was mixed with propionaldehyde, but not when *gem*-dithiols were mixed with cyclohexanone.

(b).—Boron fluoride etherate (1.1 ml.) was added dropwise with swirling to an equimolar mixture of 20.0 g. of 3,5,5-trimethyl-1,1-hexanedithiol and 6.06 g. of propionaldehyde at 0–10°. The mixture at once became cloudy because of water formation. After 24 hours, water and ether were added and the ether layer was distilled to give 21.2 g. of a complex mixture of b.p. 39–168° (0.7 mm.).

Similar results were obtained when boron fluoride etherate was added to an equimolar mixture of 1,1-propanedithiol and either acetone or propionaldehyde. In each case, a high yield of a complex liquid, b.p. 70–140° (0.5 mm.), was obtained.

In a control experiment, a solution of 5.00 g. of boron fluoride etherate, 5.00 g. of 3,5,5-trimethyl-1,1-hexanedithiol and 5.00 g. of methanol was kept at 25° for 48 hours and then poured into ice-water. Extraction with ether followed by distillation of the extract gave 4.5 g. (90% recovery) of the dithiol.

Oxidation of 3,5,5-Trimethyl-1,1-hexanedithiol by Nitric Acid.—The *gem*-dithiol (37.4 g.) was added dropwise to 520 ml. of well-stirred, 16 *N* nitric acid at such a rate that a temperature of 95–105° was maintained. After an additional 1.5 hours at this temperature, the mixture was diluted with 600 ml. of water and extracted with ether. Treatment of the aqueous layer with barium hydroxide precipitated 38.2 g. (84% yield) of barium sulfate. Distillation of the ether extract through a 36-inch spinning-band column showed that it contained about 10 g. (36% yield) of acid A, b.p. 93–97° (6 mm.), $n^{25}D$ 1.4212, and 15 g. (49% yield) of acid B, b.p. 103–104° (6 mm.), $n^{25}D$ 1.4275, neut. equiv. 158. The infrared absorption spectrum of acid B was identical with that of a sample of 3,5,5-trimethylhexanoic acid.[18] Acid A had the composition of 2,4,4-trimethylpentanoic acid.[19]

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.1; neut. equiv., 144. Found: C, 66.8; H, 11.4; neut. equiv., 146.

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[18] A. A. Pavlic (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,470,859 (1949); W. M. Bruner, *Ind. Eng. Chem.*, **41**, 2860 (1949).

[19] F. C. Whitmore, C. I. Noll, J. W. Heyd and J. D. Surmatis, THIS JOURNAL, **63**, 2028 (1941).

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 308 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Synthesis of Pyrimidines and Pyridines from Acetylene and Nitriles

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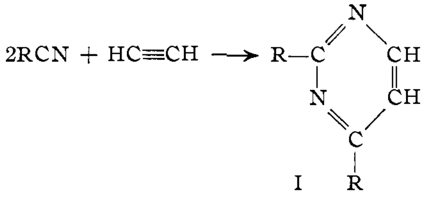
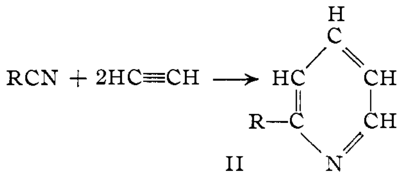
Discovery of a new reaction of acetylene with nitriles has led to synthesis of 2,4-disubstituted pyrimidines in yields up to 51%. In the propionitrile/acetylene reaction, 2,4-diethylpyrimidine and an isomeric aminopyridine were both obtained. In the benzonitrile/acetylene reaction, 2-phenylpyridine was obtained as a minor by-product.

A new reaction between acetylene and nitriles yielding principally pyrimidines and in some cases pyridines, has been discovered. Previously, pyrimidines have frequently been made by adding amidines to β-diketones or β-ketonic acids.[1] Certain alkylated pyridines have been synthesized by allowing acetylene (or acetaldehyde) to react with ammonia or hydrogen cyanide.[2,3]

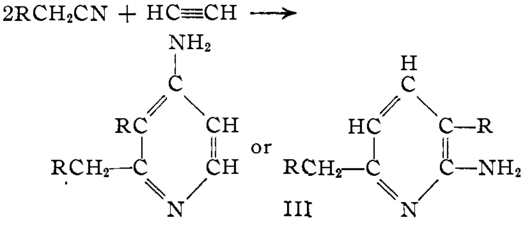
It has now been found that 2,4-disubstituted pyrimidines can be prepared in yields of up to 51%[4] from a mononitrile such as acetonitrile, propionitrile, isobutyronitrile or benzonitrile with acetylene in the presence of an alkali metal catalyst. From propionitrile, an aminopyridine isomeric with the pyrimidine was obtained in about the same yield as the pyrimidine. In the case of benzonitrile, small amounts of 2-phenylpyridine were isolated, in addition to the 2,4-diphenylpyrimidine. The reactions are illustrated by the equations



I (1)



II (2)



III (3)

The formation of these products can perhaps be best explained by means of a carbanion mechanism. Under the reaction conditions, the following ions

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[1] P. Karrer, "Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1950, pp. 818–819.

[2] J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., Waverly Press, Baltimore, Maryland, 1949, p. 60.

[3] R. C. Elderfield, "Heterocyclic Compounds," Volume I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 455.

[4] J. C. Sauer and W. K. Wilkinson, U. S. Patent 2,524,479 (1950).