presumed to be the acetoxymercurial, was crystallized from benzene.

In those preparations in which addition of sodium chloride to the reaction mixture did not result in formation of a precipitate, the solutions were concentrated to dryness at room temperature. These residues were then crystallized from suitable solvents as indicated in Table II which lists the mercurials prepared from substituted allylureas.

The N-(3-carboxymethylmercaptomercuri-2-methoxypropyl)-N'-benzoyl urea was prepared by reaction of the chloromercuri compound with thioglycolic acid in the presence of alkali as reported previously for similar compounds.[1]

Methoxymercuration of Methallylurea.—Methallylurea was mercurated similarly and the chloromercurial was prepared by addition of sodium chloride. The product after washing with water was crystallized from ethyl alcohol. The crystallized product, obtained in 55% yield, melted at 172.5–173°.

Anal. Calcd. for $C_8H_{13}N_2O_2HgCl$: Hg, 52.62; N, 7.35. Found: Hg, 52.24; N, 7.39.

Reaction of N-(3-Chloromercuri-2-methoxypropyl)-N'-benzoylurea with Dilute Alkali.—A mixture of 3.3 g. (0.007 mole) of N-(3-chloromercuri-2-methoxypropyl)-N'-benzoylurea, 30 ml. of water and 3 ml. of 10% sodium hydroxide was allowed to stand at room temperature with occasional agitation for one week. The solid was collected and washed by suspension in 50 ml. of 1% sodium hydroxide solution. The insoluble material weighed 2.9 g. (90%) and decomposed at 205–207°.

Anal. Calcd. for $(C_{12}H_{14}N_2O_3Hg)_{15}HCl$: Hg, 45.87; Cl, 0.57. Found: Hg, 45.57; Cl, 0.43.

Hydrolysis of N-(3-Chloromercuri-2-methoxypropyl)-N'-acetylurea.—A mixture of 1.0 g. (0.0024 mole) of N-(3-chloromercuri-2-methoxypropyl)-N'-acetylurea, 2.0 g. (0.005 mole) of 10% sodium hydroxide and 17 ml. of water was allowed to stand one week. To the solution was added 3.0 ml. of glacial acetic acid and after 20 hours the precipitate was collected. The product weighed 0.33 g. (35%) and melted at 152–153°. Mixed melting points with 3-chloromercuri-2-methoxypropylurea and with N-(3-chloromercuri-2-methoxypropyl)-N'-acetylurea were 152–153° and 142–152°, respectively.

MILWAUKEE, WIS. RECEIVED FEBRUARY 9, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, AND MELLON INSTITUTE]

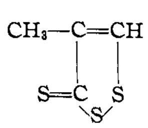
Some New Alkyl 1,2-Dithia-4-cyclopentene-3-thiones[1a]

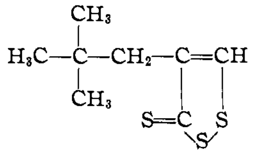
BY RODERICK S. SPINDT,[1b] DONALD R. STEVENS[1b] AND W. E. BALDWIN[1c]

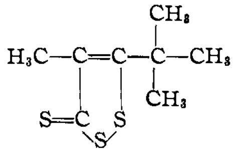
Isobutylene and diisobutylene were sulfurized with elemental sulfur to give orange crystalline compounds, $C_4H_4S_3$ and $C_8H_{12}S_3$. There were two isomers of the latter. The structures of these were determined by physical and chemical approaches. Most significant were the results obtained on alkaline hydrolysis, which gave characteristic degradation products. It was concluded that the compounds are derivatives of 1,2-dithia-4-cyclopentene-3-thione.

During a study of the reaction of sulfur with diisobutylene (a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene) an orange-colored crystalline material was isolated, from which there were obtained by fractional crystallization two isomeric compounds, each having the empirical formula $C_8H_{12}S_3$. The reaction of sulfur with isobutylene produced another orange-colored crystalline compound possessing the empirical formula $C_4H_4S_3$.

Evidence is presented in this paper to support the following structures for these compounds[2]


I


II


III

PHYSICAL PROPERTIES

	I	II	III
M.p., °C.	40.5–41.5	86.5–87.3	80.5–81.3
B.p., °C. (mm.)	110–112 (1.7)	159 (1.7)	175 (5)
d^{20}_4	1.466 ± 0.015	1.177 ± 0.018	1.359 ± 0.014

The compounds are soluble in the common organic solvents, particularly chloroform, ether and carbon disulfide, but are almost insoluble in water. They are quite soluble in concentrated inorganic acids, from which they can be recovered by dilution with water.

All three show some of the characteristics of many other organic sulfur compounds, forming methiodides with methyl iodide and yielding addition products with mercuric chloride. They are readily oxidized or reduced. They do not give a positive test for the sulfhydryl group.

Lüttringhaus, Konig and Böttcher[3] reported the preparation and characterization of a similar group of compounds obtained by treating sulfur with a number of aromatic-substituted olefins, such as 1-phenyl-1-propene, 1-phenyl-2-propene, 2-phenylpropene, etc. They gave evidence for the same ring system reported here, and described the preparation of the parent compound, $C_3H_2S_3$, by reaction of sulfur with propylene.

Other workers in this field who produced sulfur compounds of the same type are Gaudin and Pottier,[4] working with anethole; Lozac'h,[5] with

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[1] (a) Part of a thesis submitted to the Graduate School of the University of Pittsburgh by R. S. Spindt in partial fulfillment of the requirements for the degree of Doctor of Philosophy; (b) Gulf Research & Development Company's Multiple Fellowship at Mellon Institute; (c) University of Pittsburgh.

[2] Compound I was first produced by Donald R. Stevens and Arthur C. Whitaker, and II and III were first produced by Donald R. Stevens and William C. Starnes at Gulf Research & Development Co. Laboratories, Harmarville, Pa.

[3] B. Böttcher and A. Lüttringhaus, *Ann.*, **557**, 89 (1947); A. Lüttringhaus, H. B. Konig and B. Böttcher, *ibid.*, **560**, 201 (1947).

[4] O. Gaudin and R. Pottier, *Compt. rend.*, **224**, 479 (1947).

[5] N. Lozac'h, *Bull. soc. chim. France*, 840 (1949).

eugenol and related compounds; Schmitt and Lespagnol,[6] with aromatic substituted propylenes; and Voronkov, Broun and Karpenko,[7] with unsaturated aromatic hydrocarbons.

It is likely that additional compounds of this type have been prepared but not recognized, for example, the $C_5H_6S_3$, melting at 95.5°, prepared from isoprene and sulfur by Barbaglia.[8] Presumably, Selker and Kemp[9] also made it by the sulfurization of 2-methyl-2-butene in their study of the vulcanization of rubber. The present authors also prepared this compound by sulfurizing 2-methyl-2-butene and found its ultraviolet spectrum to be characteristic of the absorption system described in this paper.

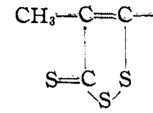
Patterson and Capell[10] lists the above ring system as 1,2-dithia-4-cyclopentene as preferred nomenclature; I, for example, would be 4-methyl-1,2-dithia-4-cyclopentene-3-thione.

In most low-temperature reactions of sulfur with hydrocarbons no rearrangement of the carbon skeleton has been reported. For this reason it was assumed and later shown that the products obtained by allowing sulfur to react with isobutylene and diisobutylene retained the same carbon skeleton found in the parent olefins.

Infrared absorption gives evidence for a carbon–carbon double bond and a thione group in each of these compounds. The wave length observed for the absorption due to a C=C bond was in the region 6.00–6.25 μ and the wave length observed for absorption due to a C=S bond was in the region 6.45–6.65 μ.

The ultraviolet spectra of these compounds are remarkably similar. The data were obtained with a Beckman spectrophotometer[11] by dissolving the pure compounds in isoöctane at a concentration of about 3×10^{-5} mole per liter. The spectra for I, II and III and for the $C_5H_6S_3$ compound (melting at 95.5°, prepared by sulfurizing 2-methyl-2-butene at 180°) are shown in Fig. 1.

Because the ultraviolet spectrum of the $C_5H_6S_3$ compound obtained from 2-methyl-2-butene is so nearly identical with the spectrum of III, it is believed that the two compounds have similar structures. Therefore, the compound $C_5H_6S_3$ is probably



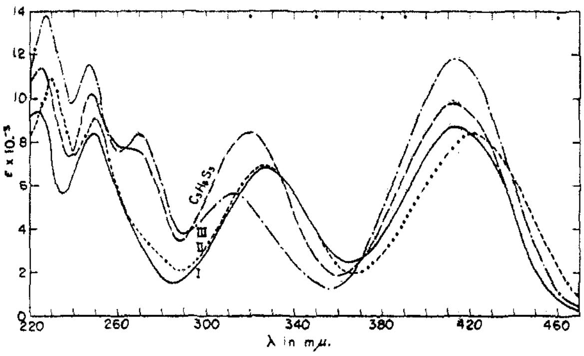
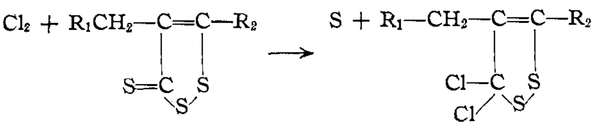


Fig. 1.

If it were the 4-ethyl derivative, the spectrum would be expected to duplicate that of I or II more closely. If it were a malonic or succinic acid derivative, the spectrum should reveal no particular resemblance to those reported here.

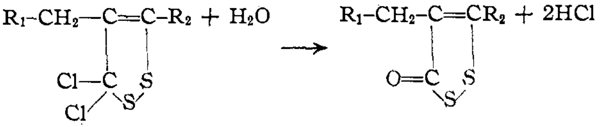
That the structures proposed are sufficient to explain all the reactions which compounds I, II and III undergo, is disclosed by the following considerations.

Chlorination of the compounds in glacial acetic acid eliminates sulfur and produces the dichlorodesthio compounds



I IVa, R_1 = H, R_2 = H
II IVb, R_1 = *t*-Bu, R_2 = H
III IVc, R_1 = H, R_2 = *t*-Bu

When the chlorination reaction was not carried to completion, evidence was obtained for an adduct in which one molecule of chlorine coupled two molecules of the compound. That both the chlorines of the dichloro compound are on one carbon atom is deduced by hydrolysis to a carbonyl compound, the oxo derivative of II and of III.



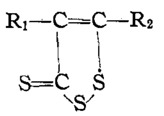
IVb Vb, R_1 = *t*-Bu, R_2 = H
IVc Vc, R_1 = H, R_2 = *t*-Bu

Little is known with certainty about the mechanism of the alkaline hydrolysis of these compounds. The following equations show the products that have been obtained from the hydrolysis reaction after various treatments.

It is evident from these equations that cleavage of the ring may occur at several points. The fragments that have been isolated and identified account for all the atoms in the parent compounds.

The assignment of cyclic structures is based on the monomolecular weights of the compounds, the finding of dimethyl disulfide (in the hydrolysis products), which suggests a disulfide linkage in the parent compounds, and the assumption that there has been no change in the carbon skeleton on sulfurization.

The best interpretation of these data supports the ring structure



This system has a formal resemblance to a dithia ester as well as to an enol derivative of a β-keto

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[6] J. Schmitt and A. Lespagnol, *Compt. rend.*, **230**, 551 (1950).

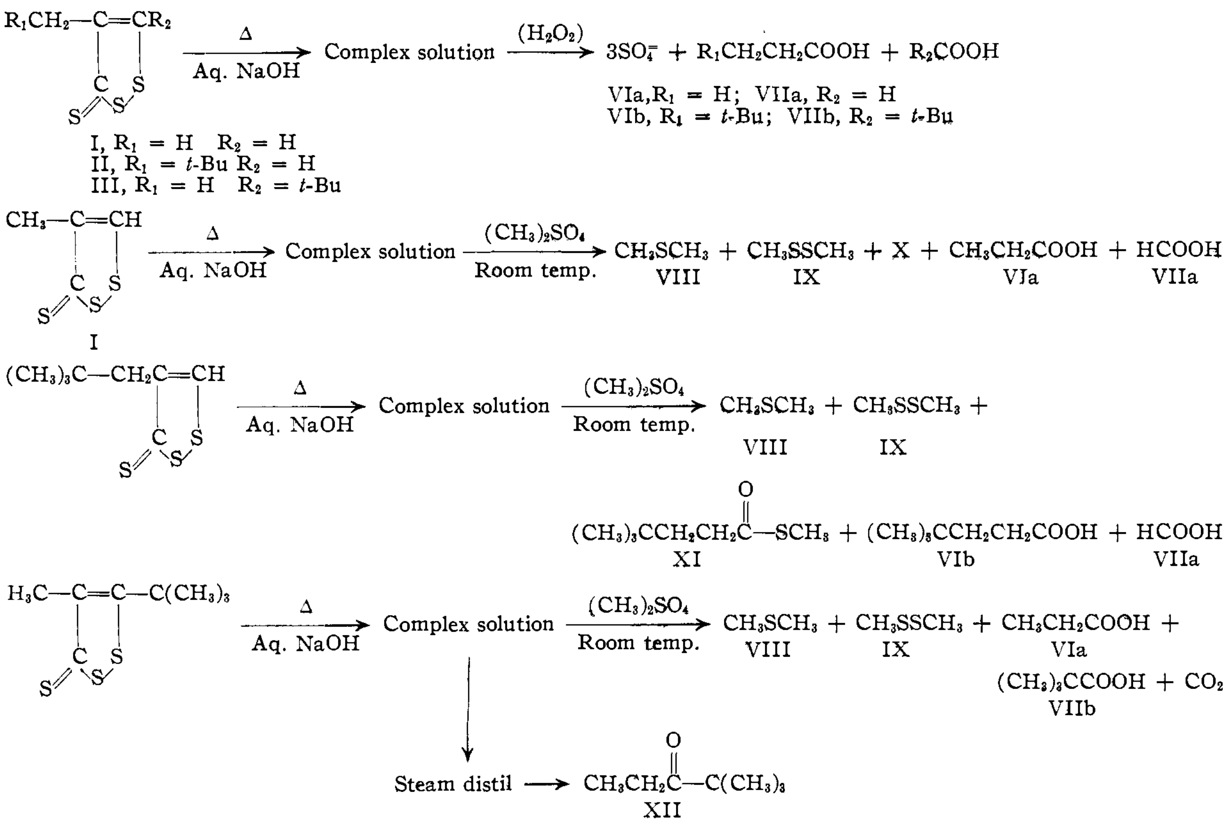
[7] M. G. Voronkov, A. S. Broun and G. B. Karpenko, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **19**, 1927 (1949); *C. A.*, **44**, 1955 (1950).

[8] G. A. Barbaglia, *Gazz. chim. ital.*, **16**, 426 (1886).

[9] M. L. Selker and A. R. Kemp, *Ind. Eng. Chem.*, **39**, 895 (1947).

[10] Austin Patterson and L. T. Capell, "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940, p. 43.

[11] By N. D. Coggeshall, Gulf Research & Development Co., Harmarville, Pa.



ester. It is this structure that accounts for the hydrolytic cleavage of the compounds by alkali. Other structures can be written but they will not account, without unwarranted assumptions, for the products that have been found.

Experimental Preparation

The stoichiometric equation for the preparation of these compounds, taking the isobutylene–sulfur reaction as an example, is

$$i\text{-}C_4H_8 + 5S \longrightarrow C_4H_4S_3 + 2H_2S$$

A side reaction between the hydrogen sulfide liberated and unreacted olefin to form *t*-butyl mercaptan makes it necessary to supply an excess of olefin to obtain an optimum yield of the $C_4H_4S_3$. The reaction is further complicated by a reaction between the mercaptan and elemental sulfur to form di- and polysulfides. Undoubtedly other side reactions also take place.

A high-pressure rotating stainless steel bomb[12] was used in this work, employing temperatures ranging from 160 to 270° and time intervals of from 30 minutes to 10 hours.

Preparation of I.—In a typical experiment, 224 g. of isobutylene (4.0 moles) was charged to the bomb containing 160 g. of sulfur (5.0 moles). On heating, the pressure rose to 830 lb. at 165°, after which the pressure dropped within 20 minutes to 200 lb. The bomb was held at 170° for 50 minutes.

The dark-brown liquid reaction product was distilled to remove low boiling by-products. The residue was then distilled and the material collected between 65 and 98° at 0.5 mm. pressure was crystallized from a 50% solution in ether at −60°. Orange needle-shaped crystals were obtained, and recrystallized from an equal volume of ethyl ether and pentane to give a yield of 57 g. of I: (m.p. 40.5–41.5°, b.p. 110–117° at 1.7 mm., d^{20}_4 −1.466 ± 0.015); a 38.5% yield based on the sulfur.

Anal. Calcd. for $C_4H_4S_3$: C, 32.43; H, 2.70; S, 64.92; mol. wt., 148.2. Found: C, 32.44, 32.64; H, 2.80, 2.92; S, 64.86, 64.94; mol. wt. (Rast), 145, 156.

Preparation of II and III.—In a typical run, 336 g. of diisobutylene (3.0 moles) and 240 g. of sulfur (7.5 moles) were heated in the bomb at 210° for 25 minutes. A maximum pressure of 150 lb. was developed and remained constant throughout the run. The product was a viscous dark-colored liquid containing unreacted sulfur. Free sulfur was always found, even in those experiments involving a large excess of diisobutylene. Because of this fact the practice was adopted of employing diisobutylene and sulfur in the molar ratio of 2.0 to 5.0. The dark-colored liquid was separated from the unreacted sulfur by treating with 50 volume per cent. of ethyl ether. An equal volume of pentane was added to the filtrate, which was then cooled at −60° to separate 168 g. of orange-colored crystals. Recrystallization from equal volumes of diethyl ether and pentane at −60° gave a mixture of II and III, melting over the range of 40 to 55°.

Fractional crystallization of this mixture slowly from an ether–pentane solution gave a precipitate rich in II. Further recrystallization of this precipitate gave pure II (m.p. 86.5–87.3°).

Anal. Calcd. for $C_8H_{12}S_3$: C, 47.00; H, 5.92; S, 47.24; mol. wt., 204.4. Found: C, 47.13, 47.18; H, 6.03, 6.06; S, 47.15, 47.28; mol. wt., 207.8.

Further cooling the ether–pentane mother liquor yielded mixed crystals. No further separation could be made from this solvent; but, when chloroform was then employed, a precipitate rich in III was obtained on slow cooling. Recrystallization from chloroform or ether yielded pure III (m.p. 80.5–81.3°).

Anal. Calcd. for $C_8H_{12}S_3$: C, 47.00; H, 5.92; S, 47.24; mol. wt., 204.4. Found: C, 47.16, 47.09; H, 6.01, 6.08; S, 47.03, 47.08; mol. wt., 210.7.

It was suspected at first that II and III were direct sulfurization products of the two hydrocarbon isomers contained in diisobutylene, namely, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. To determine whether this assumption was correct, diisobutylene was fractionated into its pure isomers and each isomer was sulfurized separately. It was found that essentially equal amounts of II and III were obtained from each of the isomeric olefins.

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[12] J. B. McKinley, THIS JOURNAL, 67, 1455 (1945).

From	Yield, %	
	II	III
2,4,4-Trimethyl-1-pentene	17.2	10.9
2,4,4-Trimethyl-2-pentene	20.6	10.3

Apparently the position of the double bond in the original diisobutylene isomers is unimportant in directing the distribution of the two compounds.

Experimental Characterization

Methyl Iodide Adduct of I.—A solution of 0.8 g. (0.005 mole) of I in 5 ml. of 95% ethanol mixed with 1.0 g. of methyl iodide gave an immediate precipitate. The product was recrystallized from 10 ml. of hot 95% ethanol to give light yellow needles melting sharply at 175°.

Anal. Calcd. for $C_5H_7S_3I$: C, 20.71; H, 2.42; S, 33.16; I, 43.71. Found: C, 21.18, 20.98; H, 2.65, 2.64; S, 33.6; I, 44.2.

Methyl Iodide Adduct of II.—The same procedure applied to II gave light yellow crystals (m.p. 157–158°).

Anal. Calcd. for $C_9H_{15}S_3I$: C, 31.20; H, 4.32; I, 36.7. Found: C, 31.33, 31.46; H, 4.21, 4.42; I, 36.0.

Methyl Iodide Adducts of III.—A solution of 10.4 g. (0.05 mole) of III in 75 ml. of ethanol refluxed with 28.4 g. (0.20 mole) of methyl iodide for 20 hours and then cooled to 0° yielded 10.9 g. of the monoaddition product. When this material was recrystallized from ethanol, bright orange diamond-shaped crystals were obtained (m.p. 148–149°).

Anal. Calcd. for $C_9H_{15}S_3I$: C, 31.20; H, 4.32. Found: C, 31.05, 31.15; H, 4.40, 4.40.

The mother liquor from the above reaction, kept at room temperature for an additional 20 hours, yielded a second crystalline material. This product, recrystallized from hot ethanol, formed dark red needles (m.p. 149–149.5°). The melting point of a mixture of the two compounds was 125°, evidence that they are not identical.

Anal. Calcd. for $C_{13}H_{24}S_5I_4$: C, 18.40; H, 2.85; I, 59.8. Found: C, 18.23, 18.28; H, 2.80, 2.88; I, 59.4, 59.6.

Chlorination of I.—Chlorination of 29.6 g. (0.2 mole) I in 400 ml. of glacial acetic acid at room temperature precipitated a white, amorphous material, tentatively identified as a monochlorine adduct. This material had a sulfur to chlorine ratio of three to one. Continued chlorination resulted in the solution of the first product and the precipitation of sulfur. The mixture was separated from the sulfur and cooled to 10° to crystallize a second white product which was filtered and washed with 200 ml. of ethyl ether in three portions. The crystals, after drying in a desiccator over calcium chloride, melted at 160.5–161°.

Anal. Calcd. for $C_4H_4S_2Cl_2$: Cl, 37.9; S, 34.3. Found: Cl, 38.0; S, 33.9.

No further data were obtained with this material.

Preparation of IVb.—Chlorination of 10.2 g. (0.05 mole) II in 200 ml. of glacial acetic acid gave a light yellow solution with the separation of sulfur. The filtered solution was cooled to 10° to yield a precipitate of white crystals. These were recrystallized from acetic acid, washed with 400 ml. of ethyl ether and dried in a desiccator (m.p. 182–183° with decomposition).

Anal. Calcd. for $C_8H_{12}S_2Cl_2$: C, 39.52; H, 4.98. Found: C, 38.97, 39.08; H, 4.80, 4.89.

Hydrolysis of IVb to Vb.—The hydrolysis of IVb to Vb was accomplished by treating 10.2 g. (0.04 mole) in 60 ml. of glacial acetic acid, with 8 ml. (0.5 mole) of water at room temperature for a period of three days. Vb was obtained from a pentane solution cooled to 10° and purified by distillation (b.p. 137° at 10 mm. pressure), to yield the light yellow crystals (m.p. 54–56°).

Anal. Calcd. for $C_8H_{12}S_2O$: C, 51.10; H, 6.38; S, 34.02. Found: C, 51.26, 51.06; H, 6.34, 6.26; S, 33.85, 33.81.

Preparation of IVc.—Chlorination of III, 20.4 g. (0.10 mole) in 50 ml. of glacial acetic acid resulted in a light yellow solution followed by precipitation of sulfur. The filtered solution was diluted with 70 ml. of ethyl ether and cooled to 0°, when a precipitate of fine needles was obtained which were filtered, washed with three 50-ml. portions of ethyl ether, placed in a desiccator and evacuated to 1 mm. pressure for three hours. A 68% yield, 16.5 g., of bright yellow crystals was obtained (m.p., sintered at 209°, decomposed at 223°).

Anal. Calcd. for $C_8H_{12}S_2Cl_2$: C, 39.52; H, 4.98. Found: C, 39.60, 39.70; H, 5.10, 5.15.

Hydrolysis of IVc to Vc.—Treatment of 120 ml. of glacial acetic acid containing 80 g. (0.33 mole) of IVc and 20 ml. (1.11 moles) of water at room temperature for one day followed by dilution with 600 ml. of water and extraction with two 200-ml. portions of pentane yielded the expected compound. It was purified by distillation (b.p. 142–143° at 10 mm. pressure, m.p. 35–36°).

Anal. Calcd. for $C_8H_{12}S_2O$: C, 51.10; H, 6.38; S, 34.02. Found: C, 51.17, 51.15; H, 6.25, 6.29; S, 33.71, 33.77.

Degradation of I by Alkaline Hydrolysis (a) Analysis and Identification of the Acidic Degradation Products.—Refluxing a mixture of 14.82 g. (0.100 mole) I and 32.0 g. (0.800 mole) sodium hydroxide in 500 ml. of water for about six hours resulted in a very dark opaque solution. The product was steam distilled to remove about 200 ml. and the residual solution was transferred to a 500-ml. volumetric flask. This solution liberated hydrogen sulfide when acidified. Attempts to determine the concentration of sulfide ion present in solution by any of several procedures gave indefinite results. This was true for each of the compounds examined.

The residual solution was decolorized by oxidation with 30% hydrogen peroxide. The total amount of acid formed, determined by titration of the oxidized mixture, was 6.75 moles. It was found that 2.33 moles of the 3.00 moles of sulfur were recovered as sulfate ion and 0.89 mole of formic acid was identified by reduction of mercuric ion. From the mixture propionic acid was also isolated (b.p. 136–137° at 740 mm. pressure; calcd.: neut. equiv., 74.1; found: neut. equiv., 75.2, 75.6).

The *p*-toluidide was prepared by the method of McElvain[13] (m.p. 125–126°, reported 125–126°).

(b) Methylation of the Sulfur-Containing Degradation Products.—Two-tenths mole (29.6 g.) of I was hydrolyzed by refluxing with alkali. The cooled solution was methylated with 126 g. (1 mole) of dimethyl sulfate in 100 ml. of diethyl ether.

Three phases were present in the mixture, including a red crystalline precipitate (X) that was partially soluble in the ether. The mixture was filtered and the separated ether solution was cooled to 0° to yield a further precipitate of X which was combined with that previously obtained. The crystals were purified by recrystallizing from ether (m.p. 154–155°).

Anal. Calcd. for $C_8H_{16}S_3$: C, 46.12; H, 7.74; S, 46.14; mol. wt., 208.4. Found: C, 47.14, 47.16; H, 5.25, 5.40; S, 45.28, 45.19; mol. wt., 208.4, 207.8. This compound has not been further identified.

The ether filtrate was dried and fractionated to yield an ether solution containing a highly odorous compound which gave a white precipitate of trimethyl sulfonium iodide–HgI_2 complex. An additional small amount of material was obtained on carrying the distillation up to 107°, at which temperature the pot residue began to decompose. This distillate also gave a precipitate when treated with methyl iodide and mercuric chloride in ethanol solution. This is evidence that the compounds in the distillate are dimethyl sulfide and dimethyl disulfide.

Degradation of II by Alkaline Hydrolysis (a) Analysis and Identification of the Acidic Degradation Products.—The hydrolysis of 0.1 mole of II was carried out using the procedure described for I. Oxidation of a 50-ml. portion of the hydrolyzed solution and analysis for acid residues were also performed in the same manner.

Total acid concentration per mole of II was 7.96 moles, very nearly theoretical for the formation of three moles of sulfuric acid and two moles of organic acids. Of the three atoms of sulfur, 2.96 atoms were recovered as sulfate ion. Formic acid, determined by reduction of mercuric ion, was recovered to the extent of 0.96 mole. On the basis of the total acid found, 1.00 mole of another organic acid was present.

The second organic acid isolated distilled at 211–212° at 745 mm. pressure.

Anal. Calcd. for $C_7H_{16}O_2$: C, 64.54; H, 10.85; neut. equiv., 130.2. Found: C, 63.90, 64.08; H, 10.99, 11.10; neut. equiv., 131.4, 131.6.

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(13) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Company, New York, N. Y., 1945, p. 184.

It was identified as 4,4-dimethylvaleric acid by conversion to the amide, which was done by first preparing the acid chloride with thionyl chloride and then treating the reaction product with aqueous ammonia. The amide, recrystallized from water, melted at 139.5-140°; reported m.p. 140-141°.[14]

Anal. Calcd. for $C_7H_{15}NO$: C, 65.06; H, 11.70; N, 10.85. Found: C, 64.81; H, 11.22; N, 10.32, 10.47.

(b) **Methylation of the Sulfur-Containing Degradation Products.**—Methylation of the hydrolyzed II was carried out by the same procedure used for I. The ether solution yielded one fraction which distilled at 109-112° at 744 mm., $n^{20}D$ 1.5230. The reported values for dimethyl disulfide are: b.p. 110° at 744 mm.; $n^{20}D$ 1.52599.

Anal. Calcd. for $C_2H_6S_2$: C, 25.52; H, 6.42; S, 68.16. Found: C, 26.40, 26.60; H, 6.95, 6.85; S, 67.0, 66.7.

A second fraction was obtained which distilled at 194° at 745 mm.; $n^{25}D$ 1.4608. This was identified by analysis and by comparison with the synthesized compound as methyl 4,4-dimethylthiovalerate.

Anal. Calcd. for $C_8H_{16}SO$: C, 60.45; H, 10.06; S, 20.01; sapon. equiv., 160.3. Found: C, 60.63, 60.69; H, 10.47, 10.50; S, 20.38, 20.37; sapon. equiv., 158.9, 161.2.

Synthesis of Methyl 4,4-Dimethylthiovalerate.—To prove that the compound obtained by methylation of the hydrolyzed II and which distilled at 194° (745 mm.) was methyl 4,4-dimethylthiovalerate, this compound was synthesized and the physical properties of the two materials compared.

The acid chloride was prepared by refluxing 13 g. (0.1 mole) of the acid with thionyl chloride and distilling the product (b.p. 145-152°).

The thio ester was prepared by treating a solution of 6 g. (0.13 mole) of methyl mercaptan in 7.9 g. (0.1 mole) of pyridine at −30° with 8.5 g. (0.05 mole) of 4,4-dimethylvaleryl chloride. The isolated methyl ester distilled at 195° at 745 mm.; $n^{25}D$ 1.4570.

Anal. Calcd. for $C_8H_{16}SO$: C, 60.45; H, 10.06; S, 20.01. Found: C, 60.75, 60.76; H, 10.41, 10.41; S, 20.26, 20.23.

Degradation of III by Alkaline Hydrolysis (a) Analysis of the Acidic Degradation Products and Isolation of a Ketone.—The quantitative hydrolysis of III was performed, using the same procedure given for I. Part of the hydrolysate was oxidized and analyzed for acid residues. The total acid found was 7.47 moles per mole of compound. Of the three sulfur atoms, 2.53 were recovered as sulfate ion. The total organic acid found was 1.6 moles, none of which was formic acid.

The original steam distillate, after hydrolysis, contained ethyl *t*-butyl ketone which was recovered by extracting the solution with three 50-ml. portions of pentane. The recovered ketone distilled at about 110° at 735 mm.; it was identified by conversion to the following three derivatives according to the procedure given by McElvain.[13]

The oxime was obtained as white crystals from water, m.p. 83.5-84.5°; reported m.p. 84.5-85.5°.[15]

The semicarbazone was obtained as white crystals from water, m.p. 147.5-148.5°; reported m.p. 144°.[15]

Anal. Calcd. for $C_8H_{17}N_3O$: C, 56.14; H, 10.00; N, 24.54. Found: C, 55.22, 55.04; H, 9.71, 9.57; N, 23.76, 23.73.

The 2,4-dinitrophenylhydrazone was obtained as flat yellow needles from ethanol, m.p. 146.5-147.5°; reported m.p. 143.5-144.5°.[15]

Anal. Calcd. for $C_{13}H_{18}N_4O_4$: C, 53.00; H, 6.12; N, 19.08. Found: C, 52.93, 53.20; H, 6.38, 6.18; N, 18.69, 18.71.

(b) **Methylation of the Sulfur-containing Degradation Products and Identification of the Organic Acids Formed.**—To obtain the acidic degradation products and the methylated sulfur compounds, 40.8 g. (0.2 mole) of III was hydrolyzed as before. The steam-distilled hydrolysate was cooled to room temperature, covered with 100 ml. of pentane and treated with 153.6 g. (1.2 moles) of dimethyl sulfate using vigorous stirring. The pentane solution yielded dimethyl sulfide, identified by precipitation of trimethyl sulfonium iodide (m.p. 208°), and a very small fraction of impure dimethyl disulfide, which distilled at 108.5° at 730 mm., $n^{25}D$ 1.5048.

The carboxylic acids, recovered from the aqueous solution, were esterified with *n*-propyl alcohol and fractionated. *n*-Propyl propionate was found as a fraction having the following properties: b.p. 123-124° at 723 mm., $n^{20}D$ 1.3926, d^{20}_{20} 0.878. The reported values for this compound are b.p. 123.4° at 760 mm., $n^{20}D$ 1.3935, d^{20}_4 0.881.

Anal. Calcd. for $C_6H_{12}O_2$: sapon equiv., 116.2. Found: sapon. equiv., 117, 119.

The ester was hydrolyzed and the acid recovered; b.p. 139° at 738 mm.; reported b.p. 141.1° at 760 mm.

Its *p*-toluidide melted at 125-126° and did not depress the melting point of an authentic sample.

n-Propyl pivalate was also recovered by fractionation; b.p. 140° at 730 mm., $n^{20}D$ 1.3965. The ester was hydrolyzed to recover the acid, b.p. 161-165° at atmospheric pressure; reported b.p. 164° at 760 mm.

Anal. Calcd. for $C_5H_{10}O_2$: neut. equiv., 102.1. Found: neut. equiv., 102.0.

Some of this acid was esterified with ethanol and fractionated, b.p. 116° at 740 mm.; reported b.p. 118° at 760 mm.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.64; H, 10.78. Found: C, 64.85, 64.82; H, 11.04, 11.10.

The pivalic acid was also converted to the amide by first making the acid chloride and treating this in ether with anhydrous ammonia. The amide was recrystallized from hot water (m.p. 152.5-153°). A known synthetic sample of the amide melted at 152.5-154° and a mixture of the two melted at 153-154°.

PITTSBURGH, PENNA. RECEIVED SEPTEMBER 25, 1950

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[14] Ch. Moureau and R. Delange, *Compt. rend.*, **136**, 552 (1903).

[15] F. C. Whitmore, C. I. Noll and V. C. Meunier, THIS JOURNAL, **61**, 683 (1939).