

80 ml of nitromethane was added, in 10 min, to a stirred refluxing slurry of 2.30 g (0.012 mole) of tetrahydrobenzo[*g*]thiochroman-4-ol (16) in 100 ml of acetic acid. After refluxing for an additional 15 min the nitromethane was removed *in vacuo* and the resulting reddish brown precipitate (4.1 g, mp 140–148°) was collected by filtration. The liquors were then concentrated to ca. 20 ml and treated with 100 ml of dry ether to give a second crop of 2.0 g, mp 135–140°. Recrystallization of the first crop from acetic acid revealed it to be trityl perchlorate, mp 141–150° dec (lit.²² mp 143–144°), while recrystallization of the second crop yielded 1.2 g (33%) of greenish brown crystals, mp 190–195° dec. Recrystallization of the second crop repeatedly from acetic acid gave an analytical sample of bright gold-green crystals of 4, mp 204–206° dec.

Anal. Calcd for C₁₃H₁₃ClO₄S: C, 51.91; H, 4.36; S, 10.66. Found: C, 51.70; H, 4.33; S, 10.62.

The ultraviolet-visible spectrum showed $\lambda_{\max}^{1\% \text{ HClO}_4 \text{ in CH}_2\text{CN}}$ 269 m μ (log ϵ 4.53), 358 (3.96), 405 (3.63).

Benzo[*g*]thiochroman-4-one (17).—A solution of 6.81 g (0.030 mole) of dicyanodichloroquinone in 75 ml of warm benzene was added slowly to a refluxing, stirred, solution of 2.18 g (0.010 mole) of 6,7,8,9-tetrahydrobenzo[*g*]thiochroman-4-one (15)^{10,11} in 25 ml of benzene. The initial green solution gave way to a brown precipitate on refluxing for 1 hr. The resulting mixture was cooled, the precipitate was filtered off, and the benzene solution was evaporated to ca. 10 ml, and then treated with petroleum ether (bp 30–40°). The resulting brown precipitate was treated with 10% aqueous base to give yellow solid which was collected and air dried to yield 0.77 g (36%) of product, mp 111–118°. The benzene-petroleum ether liquors were evaporated to dryness and treated with 10% aqueous base to yield a second crop of 0.50 g (23%), mp 88–106°. Recrystallization of this crop from petroleum ether (bp 60–70°) gave 0.45 g of yellow product, mp 115–119°. A sample of the first crop, recrystallized from petroleum ether (bp 60–70°), sublimed at 100° (0.05 mm), recrystallized, and then resublimed, had a melting point of 121–123°.

Anal. Calcd for C₁₃H₁₀OS: C, 72.87; H, 4.71; S, 14.97. Found: C, 72.96; H, 4.80; S, 15.03.

An nmr spectrum of 17 in CDCl₃ exhibited an A₂X₂ multiplet of ten peaks (4 H of H-2 and H-3) centered at δ 3.15, aromatic singlets at 8.62 (H-5), and 7.65 (H-10) as well as normal aromatic peaks (4 H) in the region 7.27–7.90.

Benzo[*g*]thiochroman-4-ol (18).—A solution of 1.95 g (0.0091 mole) of benzo[*g*]thiochroman-4-one (17) in 150 ml of warm, dry ether was added dropwise to a stirred slurry of 1.50 g (0.040 mole) of lithium aluminum hydride in 125 ml of ether during 0.5 hr. After being stirred for 1 hr the solution was cautiously hydrolyzed by the addition of 10 ml of ethyl acetate followed by 10 ml of water. The lithium salts were removed by filtration and the filtrate was dried (MgSO₄) and evaporated to dryness. The resulting white solid was recrystallized from 500 ml of petroleum ether (bp 60–70°) to yield 1.72 g (87%) of yellow product, mp 118–121°. Sublimation at 100° (0.1 mm) gave an analytical sample as white needles, mp 120–122°.

Anal. Calcd for C₁₃H₁₂OS: C, 72.19; H, 5.59; S, 14.82. Found: C, 72.35; H, 5.66; S, 14.84.

Registry No.—1, 3220-72-2; 2, 10147-15-6; 3, 10181-99-4; 4, 10137-42-5; 5, 7432-90-8; 6, 7432-91-9; 7, 7432-92-0; 8, 7432-93-1; 9, 2567-20-6; 10, 7432-95-3; 11, 7432-96-4; 13, 6157-10-4; 16, 10137-50-5; 17, 10137-51-6; 18, 10137-52-7.

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Chemistry of Dimethylketene Dimer. VII. Dimers of Dimethylthioketene¹

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The reaction of tetramethyl-1,3-cyclobutanedione with phosphorus pentasulfide gives tetramethyl-1,3-cyclobutanedithione (3) and tetramethyl-3-thio-1,3-cyclobutanedione (4). These may be converted into the corresponding unsaturated β -(thio lactones), 3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid β -(thio lactone) (6) and 3-mercapto-2,2,4-trimethyl-3-pentenoic acid β -(thio lactone) (7). Pyrolysis of 3 gives a third dimer of dimethylthioketene, which is evidently 2,4-diisopropylidene-1,3-dithietane (10).

Although the chemistry of ketene and its homologs has been studied intensively for many years, the literature contains only a few references to attempts to prepare monomeric thioketene or its alkyl derivatives. In most cases these attempts were unsuccessful.² Recently, however, a process for preparing monomeric thioketene and methylthioketene was patented,³ and the synthesis and several reactions of hexafluorodimethylthioketene were reported.⁴ Earlier, Schönberg, *et al.*,^{5–7} had described the preparation of compounds of structure 1 which are dimers of diarylthioketenes.

(1) Paper VI in this series: J. C. Martin, R. D. Burpitt, and H. U. Hostetter, *J. Org. Chem.*, **32**, 210 (1967).

(2) H. Staudinger, G. Rathsam, and F. Kjelsberg, *Helv. Chim. Acta*, **3**, 853 (1920).

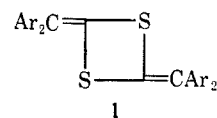
(3) E. G. Howard, Jr. (to E. I. du Pont de Nemours and Co.), U. S. Patent 3,035,030 (1962).

(4) M. S. Raasch, *Chem. Commun.*, 577 (1966).

(5) A. Schönberg, L. V. Vargha, and H. Kaltschmidt, *Ber.*, **64**, 2582 (1931).

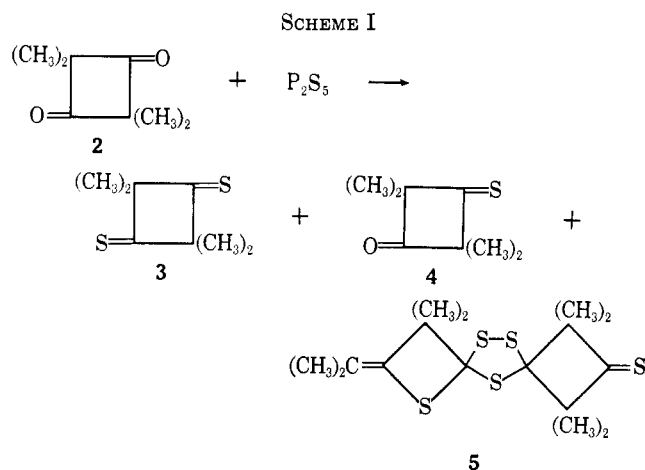
(6) A. Schönberg, A. Stephenson, H. Kaltschmidt, E. Petersen, and H. Schulten, *ibid.*, **66**, 237 (1933).

(7) A. Schönberg, E. Feese, and K.-H. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).



We prepared a dimer of dimethylthioketene, tetramethyl-1,3-cyclobutanedithione (3),^{7a} by refluxing tetramethyl-1,3-cyclobutanedione (2) with excess phosphorus pentasulfide in pyridine solution. When 3 is prepared in this way, it is accompanied by a small amount of tetramethyl-3-thio-1,3-cyclobutanedione (4), which may be regarded as a mixed dimer of dimethylketene and dimethylthioketene, a minor amount of 2-isopropylidene-1,1,7,7,9,9-hexamethyl-3,5,10,11-tetra-thiadispiro[3.1.3.2]undecane-8-thione (5), and several unidentified compounds (see Scheme I). By using

(7a) NOTE ADDED IN PROOF.—The preparation of 3 from tetramethyl-1,3-cyclobutanedione and hydrogen sulfide in the presence of hydrogen chloride and zinc chloride was reported after the work in this article had been completed [R. D. Lipscomb (to E. I. du Pont de Nemours and Co., Inc.), U. S. Patent 3,297,765 (Jan 10, 1967)].



excess **2** and stopping the reaction after about 40 min, **4** may be made the major product.

Compounds **3** and **4** are bright red crystalline solids which, unlike most other aliphatic thio ketenes,⁸ show no tendency to dimerize or polymerize at ordinary temperatures. These compounds sublime readily at room temperature and have characteristic, somewhat camphoraceous, odors.

The structure of **3** was established by its mass spectrum,⁹ nmr spectrum¹⁰ (Table I), and elemental analy-

TABLE I
NMR SPECTRA OF
(CH₃)₂—C—S—C—(CH₃)₂
X= Y

Compd	X	Y	δ, ppm ^a
2	O	O	1.31
4	O	S	1.33
3	S	S	1.40

^a Nmr spectra were recorded on carbon tetrachloride solutions. See footnote 10.

sis. The 2,4-dinitrophenylhydrazone and bis(2,4-dinitrophenylhydrazone) of **3** were also prepared and identified; the latter was identical with the bis(2,4-dinitrophenylhydrazone) of **2**. Attempts to obtain good values for the molecular weights of **3** and **4** by either ebulliometric or cryoscopic methods were unsuccessful. However, the values obtained were sufficiently close to the theoretical values to indicate that **3** and **4** are monomeric; this indication was confirmed by the position of the parent peaks in the mass spectra of **3** and **4** at *m/e* 172 and 156, respectively. The nmr spectrum of **4** was also in accord with the structure shown (Table I). Additional evidence for this structure was furnished by the elemental analysis of **4** and by its infrared spectrum,¹¹ which contained a doublet at 1780 cm⁻¹. The reaction of **4** with 2,4-dinitrophenylhydrazine at room temperature gave a derivative which was identical with the 2,4-dinitrophenylhydrazone of **3**.

(8) R. Meyer, J. Morgenstern, and I. Fabian, *Angew. Chem.*, **76**, 157 (1964).

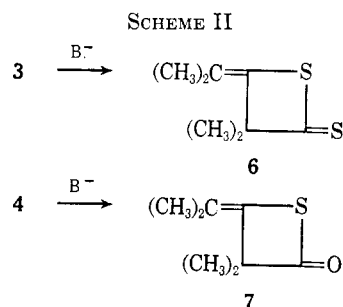
(9) Mass spectra were recorded on a Consolidated Engineering Type 21-620 instrument.

(10) Unless otherwise noted, nmr spectra were recorded on a Varian A-60 spectrometer at 60 Mc. Field position values are referred to tetramethylsilane as an internal standard.

(11) Infrared spectra were recorded on a Baird A-2 instrument, using the potassium bromide pellet method for solids and neat liquid between sodium chloride plates for liquids.

The structure of **5** was deduced from its elemental analysis, from its nmr spectrum, and by pyrolysis, which gave **3** and **6** in approximately equal amounts and also a third compound which was detected by glpc but not identified.

When **3** and **4** were heated in the presence of bases, they rearranged to the unsaturated β-lactones **6** and **7**, respectively (see Scheme II). The structures of these

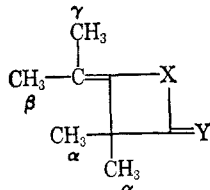


compounds, formed by addition of the C=C bond of one ketene molecule to the C=S bond of another, are analogous to those of diketene and the "lactone dimers" of substituted ketenes. The rate of this rearrangement was markedly dependent upon the nature of the reaction solvent, as well as upon the basicity of the catalyst. Although no quantitative studies were undertaken, it was found that the rearrangement of **3** to **6** was complete after heating 30 min to 70° with triethylenediamine or triethylamine in dimethyl sulfoxide. The reaction was somewhat slower in *N,N*-dimethylformamide. When the experiment was repeated in ethyl alcohol or acetonitrile, there was no reaction after a comparable period. However, sodium methoxide in refluxing benzene produced complete rearrangement within 10 min. We were surprised to find that in methanol solution **3** rearranged to **6** in good yield. Under the same conditions **2** gives methyl 2,2,4-trimethyl-3-oxovalerate in almost quantitative yield.¹² Detectable rearrangement of **4** to **7** at 70° occurred only in dimethyl sulfoxide or *N,N*-dimethylformamide solution and then only in the presence of sodium methoxide or sodium methylsulfinyl carbanion (prepared by dissolving sodium hydride in dimethyl sulfoxide).

When **3** was heated to temperatures above 125°, it rearranged slowly to **6**. An appreciable amount of **6** was also formed, together with **3**, **4**, and foul-smelling by-products, when **2** and phosphorus pentasulfide were refluxed in toluene or xylene solution. Rearrangement to **6** also occurred slowly during distillation of **3** at atmospheric pressure, and for this reason it is not practical to separate **3** from **4** completely by distillation. Therefore, in laboratory work it is preferable to perform a rough separation by rapid distillation and then to prepare pure **3** by recrystallization.

The structure of **6** was deduced from its nmr spectrum (Table II), which is very similar to that of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (**8**), and from its reaction with hydrazine, which gave 3-isopropyl-4,4-dimethyl-2-pyrazolin-5-one hydrazone. Acid hydrolysis of the latter gave 3-isopropyl-4,4-dimethyl-2-pyrazolin-5-one (**9**), identical with that pre-

(12) R. H. Hasek, E. U. Elam, J. C. Martin, and R. G. Nations, *J. Org. Chem.*, **26**, 700 (1961).

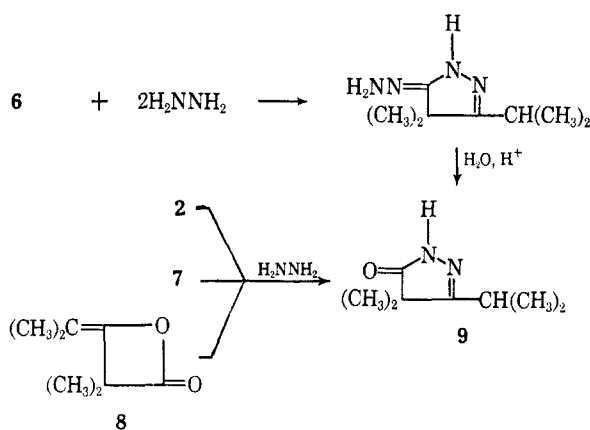
TABLE II
 NMR SPECTRA OF


Compd	X	Y	δ , ppm ^a		
			α	β	γ
8	O	O	1.47	1.64 (1.68)	1.68 (1.64)
7	S	O	1.41	1.68 (1.76)	1.76 (1.68)
6	S	S	1.41	1.70 (1.86)	1.86 (1.70)

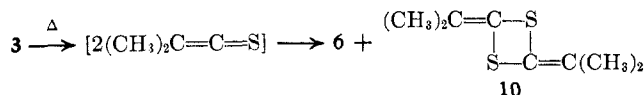
^a Nmr spectra were recorded on the pure compounds.¹⁰

pared from 2 or 8.¹³ The nmr spectrum of 7 (Table II) also resembled that of 6 and 8, and the reaction of this compound with hydrazine gave 9 (see Scheme III).

SCHEME III



Pyrolysis of 3, either over Vycor chips at 485° or in a modified ketene lamp,¹⁴ gave 6 and a 12% yield of a yellow, crystalline solid. This material, based on its elemental analysis, infrared and nmr spectra, and analogy with the dimers of diarylthioketenes,⁵⁻⁷ is believed to have structure 10. Although there was no direct evidence for the presence of monomeric dimethylthioketene in the pyrolysis products of 3, the most logical explanation for the formation of 10 is that 3 dissociates to dimethylthioketene, which then recombines to give 6 and 10. It is also conceivable that 6, but not 10, was formed by rearrangement of 3 without



complete dissociation. If dimethylthioketene is indeed an intermediate in the formation of 10, recombination must occur rapidly and at a fairly high temperature since crystals of 10 collected on the hot walls of the pyrolysis tube immediately below the furnace. Pyrolysis of 6 under these conditions did not give 10.

Experimental Section^{15,16}

Tetramethyl-1,3-cyclobutanedithione (3) and 2-Isopropylidene-1,1,7,7,9,9-hexamethyl-3,5,10,11-tetrathiadispiro[3.1.3.2]undec-

(13) R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 4340 (1961).

(14) W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 136 (1946).

ane-8-thione (5).—A solution of 300 g (2.1 moles) of 2 in 1 l. of pyridine was stirred and refluxed with 454 g of phosphorus pentasulfide until the reaction of 2 was complete as indicated by glpc (1.5 hr). The mixture was cooled, and the liquid was decanted. The residue was extracted by heating it with two 200-ml portions of pyridine to refluxing temperatures. The combined pyridine solutions were distilled rapidly through a short Vigreux column at 100 to 150 mm until most of the pyridine had been removed from the mixture and a solid material appeared in the column. The residue was taken up in hot methanol, and the solution was decanted from a small amount of insoluble material. The distillate was combined with the methanol extract of the residue, and the pyridine and the methanol were removed by fractionation through a 4-ft column packed with 0.16 × 0.16 in. protruded packing until the base temperature reached 60° (30 mm). The distillation residue was cooled to room temperature and filtered. One recrystallization of the product from methanol gave 182 g (50%) of crude 3, mp 109–119°. Repeated recrystallizations from methanol yielded an analytical sample: mp 123.5–125°; infrared absorptions at 1460, 1265, and 1075 cm⁻¹; nmr spectrum (CCl₄), singlet at 1.40 ppm; ultraviolet absorptions, $\lambda_{\text{max}}^{\text{hexane}}$ 227 m μ (ϵ 21,600) and 298 m μ (ϵ 409). There was also a weak absorption in the visible region, $\lambda_{\text{max}}^{\text{hexane}}$ 500 m μ (ϵ 22.4). Major peaks in the mass spectrum were at *m/e* 86 (100%), 71 (54.4%), 96 (52.9%), 81 (50.8%), 45 (48.4%), and 39 (21.8%). The parent peak was located at *m/e* 172.

Anal. Calcd for C₈H₁₂S₂: C, 55.8; H, 7.0; S, 37.2; mol wt, 172. Found: C, 55.3; H, 7.1; S, 36.7; mol wt (boiling point elevation in benzene) 218, (boiling point elevation in acetone) 222, (freezing point depression of benzene) 142, 147.

The 2,4-dinitrophenylhydrazone of 3 (mp 154–156°) was prepared by treating 3 with alcoholic 2,4-dinitrophenylhydrazine at room temperature.

Anal. Calcd for C₁₄H₁₆N₄O₄S: S, 9.5. Found: S, 9.4.

The bis(2,4-dinitrophenylhydrazone) of 3 (mp 320–322° dec) after recrystallization from ethyl alcohol, was prepared by refluxing 3 with alcoholic 2,4-dinitrophenylhydrazine solution for 10 hr. This material was identical with the compound prepared similarly from 2.

Anal. Calcd for C₂₀H₂₀N₈O₈: C, 48.0; H, 4.1; N, 22.4. Found: C, 48.1; H, 4.6; N, 21.8.

The filtrate from the distillation residue and the mother liquor from recrystallization of the crude 3 were combined and concentrated on the steam bath; the concentrate was then cooled in a Dry Ice-acetone bath. Recrystallization of the solid which separated gave 11 g of a pink solid 5, mp 128°. A sample prepared for analysis by recrystallization from hexane melted at 129–130°; infrared absorptions at 1440, 1340, 1280, and 1130 cm⁻¹. The 100-Mc nmr spectrum¹⁷ showed seven peaks at 1.71, 1.63, 1.59, 1.58, 1.50, 1.46, and 1.43 ppm with area ratios of 1:1:1:1:1:1:2, indicating that the molecule contained eight methyl groups, two of which gave overlapping peaks. Under very high resolution the peak at 1.71 and the peak at 1.43 ppm were split into quartets with *J* = 0.45 cps. This same splitting occurred for the peaks corresponding to the two isopropylidene peaks in the high-resolution nmr spectra of 7 and 8¹⁸ and was taken as evidence that these methyl groups were attached to an unsaturated carbon atom. No splitting of the peak corresponding to the methyl groups of 3 was observed under these conditions. Structure 5 is consistent with the observed nmr spectrum.

Anal. Calcd for C₁₆H₂₄S₅: C, 51.0; H, 6.4; S, 42.6; mol wt, 337. Found: C, 51.1; H, 6.5; S, 42.5; mol wt (boiling elevation of acetone) 323, 336.

A small amount of 5 was placed in a test tube and heated for a few minutes over a flame. The melt turned orange-red. The product was taken up in hexane and analyzed by glpc (Carbowax 20M). Approximately equal amounts of 3 and 6, as well as a smaller amount of unidentified material with a longer retention time, were shown to be present.

Tetramethyl-3-thio-1,3-cyclobutanedione (4).—A solution of 300 g (1.35 moles) of phosphorus pentasulfide and 420 g (3 moles)

(15) Melting points were taken on a Thomas-Hoover melting point apparatus in open capillary tubes and are corrected.

(16) Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 505 instrument.

(17) The 100-Mc nmr spectra were recorded on a Varian HA-100 instrument, using tetramethylsilane as an internal standard.

(18) High Resolution NMR Spectra Catalog, Vol. 2, Varian Associates, Palo Alto, Calif., 1963.

of 2 in 1 l. of pyridine was refluxed with stirring. The progress of the reaction was followed by glpc and heating was stopped after 40 min, when it appeared that formation of 3 had become more rapid than that of 4. The hot solution was allowed to settle briefly and then the liquid was decanted. The solid was heated to boiling with 250 ml of fresh pyridine, cooled, and decanted. The combined pyridine solutions were distilled rapidly, without fractionation, at 35 to 50 mm in order to remove the last of the inorganic material. The pyridine was removed from the distillate by fractionation, at 50% takeoff, through a 4-ft column packed with 0.16 × 0.16 in. protruded packing until the base temperature reached 60° (30 mm). The distillation residue was taken up in 300 ml of warm hexane, and the solution was decanted from a small amount of tar and cooled to 20°. The 2 which separated was removed by filtration and washed with hexane until the color had been removed. The filtrate was washed with 10% sodium hydroxide until glpc indicated that all of the 3 had been removed, and then it was distilled to give 188 g of 4, bp 162–167°. The major component of the residue (99 g) from this distillation was 6.

A sample of 4 purified for analysis by preparative-scale glpc melted at 57–59°; infrared absorptions at 1800, 1770, 1450, 1290, and 1125 cm^{-1} ; nmr spectrum (CCl_4), singlet at 1.33 ppm; ultraviolet absorptions, $\lambda_{\text{max}}^{\text{hexane}}$ 228 $\text{m}\mu$ (ϵ 8650), 272 (s) (316), and 328 (117). There was also a weak absorption in the visible region at $\lambda_{\text{max}}^{\text{hexane}}$ 520 $\text{m}\mu$ (ϵ 9.65). Major peaks in the mass spectrum were located at m/e 71 (100%), 86 (98.1%), 41 (89.5%), 39 (82.7%), 27 (56.3%), and 45 (54.2%). The parent peak was located at m/e 156.

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{OS}$: C, 61.5; H, 7.7; S, 20.5. Found: C, 61.3; H, 7.5; S, 20.8.

When a solution of 4 in alcohol was treated with alcoholic 2,4-dinitrophenylhydrazine solution and allowed to stand at room temperature, the 2,4-dinitrophenylhydrazone of 3 precipitated. After recrystallization from methanol this derivative melted at 157–158°.

3-Mercapto-2,2,4-trimethyldithio-3-pentenoic Acid β -(Thio lactone) (6).—A solution of 15 g of 3 in 75 ml of benzene was treated with 0.5 g of sodium methoxide and refluxed with stirring for 15 min until the color change from red to orange was complete. The solution was acidified with formic acid, filtered, and distilled to give 11.2 g (75%) of 6: bp 112–116° (20 mm); infrared absorptions at 1235, 1160, 1070, 865, and 822 cm^{-1} ; nmr spectrum (neat), singlets at 1.41, 1.70, and 1.86 ppm. The areas of these peaks were in the ratio 2:1:1. A sample was purified for analysis by preparative-scale glpc.

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{S}_2$: C, 55.8; H, 7.0; S, 37.2; mol wt, 172. Found: C, 56.1; H, 6.9; S, 37.3; mol wt (boiling point elevation in benzene), 176.

The effect of the reaction solvent and the catalyst upon the rate of conversion of 3 to 6 was measured by dissolving 0.5 g of 3 in 10 ml of the solvent in a test tube, adding a trace of catalyst, and placing the tube in a water bath at 75°. At the end of 30 min a few drops of acetic acid was added, and the solutions were analyzed by glpc. Under these conditions 3 was almost completely converted to 6 in dimethyl sulfoxide solution in the presence of either triethylamine or diethylenetriamine or in ethyl alcohol solution in the presence of benzyltrimethylammonium hydroxide. Triethylenediamine produced almost no rearrangement in ethyl alcohol or in acetonitrile solution. Under the same conditions incomplete rearrangement was observed in dimethylformamide containing diethylenetriamine and in xylene containing benzyltrimethylammonium hydroxide.

3-Isopropyl-4,4-dimethyl-2-pyrazolin-5-one Hydrazone.—A solution of 43.5 g (0.25 mole) of 6 in 200 ml of hexane was refluxed with stirring and 24 g (0.75 mole) of hydrazine was added dropwise. A vigorous reaction occurred, and the mixture solidified. The product was recrystallized twice from ethyl acetate to give 15 g (36%) of 3-isopropyl-4,4-dimethyl-2-pyrazolin-5-one hydrazone: mp 272°; infrared absorptions at 3330, 1650 (doublet), and 1030 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{N}_2$: C, 57.1; H, 9.6; N, 33.3. Found: C, 56.5; H, 9.2; N, 33.1.

A solution of 4 g of the hydrazone in 50 ml of 10% hydrochloric acid was allowed to stand at room temperature for 24 hr, then

refluxed for 1 hr, and cooled. The crystalline product (2 g) melted at 77–79° after one recrystallization from water. The infrared spectrum was identical with that of authentic 3-isopropyl-4,4-dimethyl-2-pyrazolin-5-one.¹³

Anal. Calcd for $\text{C}_8\text{H}_{14}\text{N}_2\text{O}$: N, 18.2. Found: N, 18.2.

3-Mercapto-2,2,4-trimethyl-3-pentenoic Acid β -(Thio lactone) (7).—A solution of 1 g of a 50% dispersion of sodium hydride in mineral oil in 50 ml of dimethyl sulfoxide was added to a solution of 62.4 g (0.4 mole) of 4 in 70 ml of dimethyl sulfoxide, and the solution was warmed slightly. After the reaction was complete, the mixture was distilled rapidly to remove the catalyst, the distillate was poured into water, and the aqueous solution was extracted with two 150-ml portions of ether. The ether extracts were dried and distilled to give 31 g (50%) of 7: bp 72–73° (8 mm); n_D^{20} 1.5065; infrared absorptions at 1780, 1010, 910, 870, and 850 cm^{-1} ; nmr spectrum (neat), 1.41, 1.68, and 1.76 ppm. The areas of these peaks were in the ratio 2:1:1.

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{OS}$: C, 61.5; H, 7.7; S, 20.5. Found: C, 61.8; H, 7.7; S, 19.8.

When a small amount of 7 was shaken vigorously with excess 64% aqueous hydrazine, the mixture became hot and almost homogeneous; then it clouded and finally crystalline material separated. The crystalline material was recovered by filtration, washed with water, and dried. It melted at 77–79° and was shown by comparison of the infrared spectra to be identical with 3-isopropyl-4,4-dimethyl-2-pyrazolin-5-one prepared by the hydrolysis of 3-isopropyl-4,4-dimethyl-2-pyrazolin-5-one hydrazone or by the reaction of 2 with hydrazine.¹³

Pyrolysis of 3.—A solution of 30 g of 3 in 200 ml of hexane was passed at the rate of approximately 1 to 2 ml per min through a 1 × 12 in. tube packed with Vycor chips and heated to 485°. A stream of nitrogen was also passed through the tube during the experiment. Gases from the furnace were passed through a receiver, a water-cooled reflux condenser, and a Dry Ice cooled trap, then to the atmosphere. Glpc indicated that the product contained 6, unreacted 3, and a third component which separated as tan crystals (2.4 g, mp 160–170°) on cooling the product solution in a Dry Ice–acetone bath. The material which melted from 160 to 170° was recrystallized from acetic acid to give 10 as bright yellow crystals: mp 170–172°; infrared absorptions at 1650, 1430, 1365, 1075, and 865 cm^{-1} ; nmr spectrum (CCl_4), singlet at 1.6 ppm. An additional 1.3 g of the same product (mp 169–172°) was recovered by washing the condenser and the tubing between the furnace and the condenser with hexane.

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{S}_2$: C, 55.8; H, 7.0; S, 37.2; mol wt, 172. Found: C, 56.0; H, 6.8; S, 37.1; mol wt (boiling point elevation in benzene), 189, 193.

The mother liquor from which crude 10 had been removed was heated to 200° to remove solvent. The residue (22.5 g) was shown by glpc to consist of 6, probably contaminated with non-volatile by-products. Glpc of the small amount of material which collected in the Dry Ice trap during pyrolysis indicated that it contained very small amounts of the same compounds collected in the main receiver and nothing else. A minute amount of the product (mp 170–171°) was obtained by allowing this condensate to evaporate and then washing the residue with hexane and methanol.

Registry No.—2, 933-52-8; 3, 10181-56-3; 2,4-dinitrophenylhydrazone of 3, 10181-57-4; bis(2,4-dinitrophenylhydrazone of 3, 10181-58-5; 4, 10181-59-6; 5, 10181-60-9; 6, 10181-61-0; 7, 10181-62-1; 8, 3173-79-3; 10, 10181-64-3; 3-isopropyl-4,4-dimethyl-2-pyrazolin-5-one hydrazone, 10211-65-1.

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