[Contribution from the Research Department of Socony Mobil Oil Co.]

Synthesis and Reactions of 4-Neopentyl-5-*t*-butyl-1,2-dithiole-3-thione

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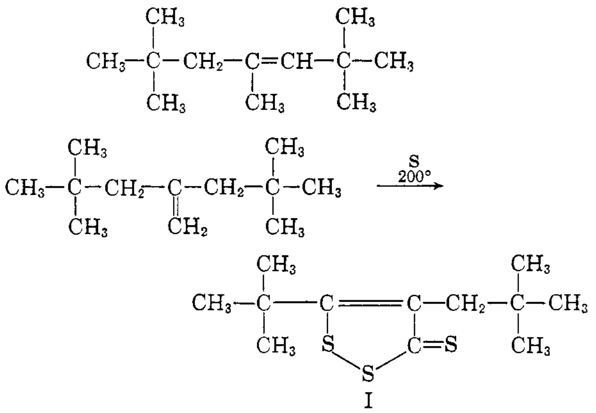
Received February 29, 1960

The reaction of sulfur with triisobutylene at 200° yields exclusively 4-neopentyl-5-*t*-butyl-1,2-dithiole-3-thione. This compound has been characterized by physical and chemical analysis, including basic hydrolysis to 2,2-dimethylpropionic and 2,2-dimethylvaleric acids. Chlorination of the thione followed by hydrolysis gives the ketone analog.

Olefins having methyl substituents or olefins which are easily converted to the methyl substituted compound are known to react with sulfur and/or phosphorus pentasulfide at elevated temperatures forming the pseudoaromatic 1,2-dithiole-3-thiones.[1] An interesting example of this reaction is the formation of a mixture of 4-methyl-5-*t*-butyl-1,2-dithiole-3-thione and 4-neopentyl-1,2-dithiole-3-thione by reaction of sulfur with diisobutylene (a mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2) at 200°.[2]

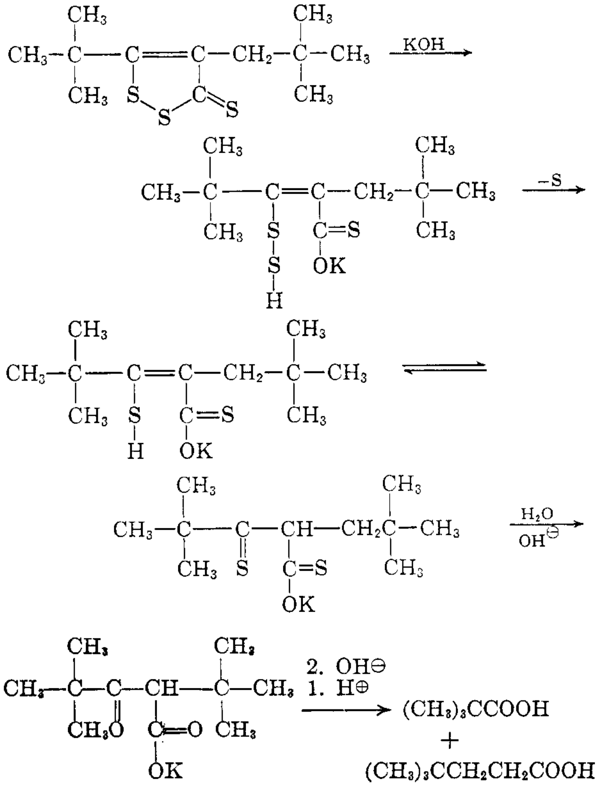
Triisobutylene is a readily obtainable olefin consisting primarily of 2,2,4,6,6-pentamethylheptene-3 and 1,1-dineopentylethylene.[3] Since terminal olefins are isomerized to the methyl compound before reaction with sulfur in the formation of 1,2-dithiole-3-thiones,[1] reaction of triisobutylene with sulfur should give only 4-neopentyl-5-*t*-butyl-1,2-dithiole-3-thione, I.



I

Reaction of triisobutylene with sulfur at 200° was carried out by dropping the olefin onto heated sulfur at atmospheric pressure. By-product hydrogen sulfide was passed out of the condensing system and measured with a Wet Test Meter in which the water had previously been saturated with hydrogen sulfide. Unchanged triisobutylene was returned to the reaction flask by means of an efficient condenser. The reaction can be facilitated by the addition of preformed sulfurized triisobutylene to the sulfur charge. This serves to reduce the viscosity of the sulfur and provides better olefin-sulfur contact, measurably increasing the rate of reaction.

Vacuum distillation of the product from this reaction gave a red oil distilling at 150–160° at 1 mm. The distilled product had a refractive index (using the hydrogen red line) of 1.6475 and its empirical formula was $C_{12}H_{20}S_3$. A 100-gram sample was fractionated under vacuum using a Piros-Glover spinning band column. Eighteen approximately equal fractions were taken. Fractions 4–15 (72% of the total distillate) had identical infrared spectra. Fractions 16–18 (10% of the total distillate) showed a small band developing at 9.92 μ. If this contaminant is an isomer of the parent sulfur compound it must be present in less than



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(1) B. Böttcher and A. Lüttringhaus, *Ann.*, **557,** 89 (1945); A. Lüttringhaus, H. Koenig, and B. Böttcher, *Ann.*, **560,** 201 (1947); N. Lozac'h, *Bull. soc. chim. France*, 840 (1949); B. Böttcher, *Ber.*, **81,** 376 (1948); M. Voronkov, A. Broun, and G. Karpenko, *J. Gen. Chem.* (*U.S.S.R.*), **19,** 1927 (1949).

(2) R. S. Spindt, D. R. Stevens, and W. E. Baldwin, *J. Am. Chem. Soc.*, **73,** 3693 (1951).

(3) F. Whitmore, *Organic Chemistry*, D. Van Nostrand Co., New York (1951), p. 49.

5% of these fractions or less than 0.5% of the total distillate.

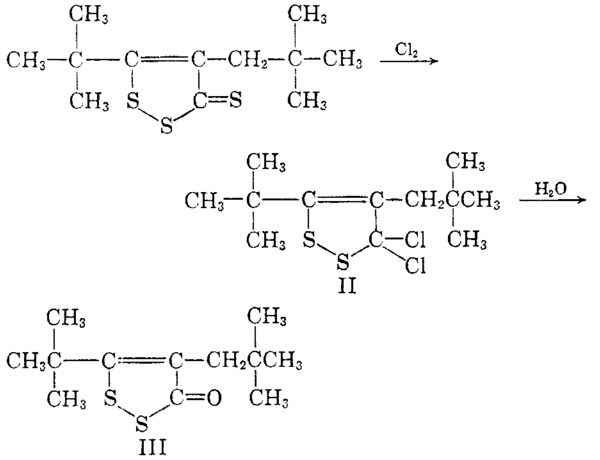
The structure of I is strongly supported by hydrolysis with alcoholic potassium hydroxide, whereby two organic acids were obtained, 2,2-dimethylpropionic and 4,4-dimethylvaleric acids.

Further support of the structure is obtained from spectra. Only two types of protons are observed in the NMR spectra of I. The methyl peak occurs as a doublet with a chemical shift (with reference to water as an external standard) of 129 and 148 cps. The doublet results from two *t*-butyl groups with different environments. The methylene peak has a chemical shift of 66 cps. The CH_3 to CH_2 proton ratio is 8.4 to one.

Ultraviolet and infrared spectra of I were obtained and compared with the ultraviolet spectra of the analogs from diisobutylene. Strong absorption maxima at 230, 248, 275, 321 and 414 mμ are characteristic of the dithiole-3-thiones and attest to the aromaticity of this structure.

A comparison of the infrared spectra of I with 4-neopentyl-1,2-dithiole-3-thione and 4-methyl-5-*t*-butyl-1,2-dithiole-3-thione was made. In all cases there is evidence for a carbon-carbon double bond, a thione group, and a carbon-sulfur bond.

Chlorination of I produced the dichloro-desthio derivative II which was readily hydrolyzed to the carbonyl compound III.



II

III

I also undergoes reactions typical of 1,2-dithiole-3-thiones. It forms oximes and hydrazones with hydroxylamine and hydrazine reagents, quaternary salts with alkyl halides, and well defined complexes with metal salts such as mercuric chloride, silver nitrate, bismuth trichloride, antimony trichloride, stannic chloride, cadmuim chloride, and lead diacetates. Nitric acid cleaves the dithiole ring yielding white solids which have not been characterized.

EXPERIMENTAL

The stoichiometric equation for the preparation of 4-neopentyl-5-*t*-butyl-1,2-dithiole-3-thione is

$$C_{12}H_{24} + 5\ S \longrightarrow C_{12}H_{20}S_3 + 2H_2S$$

It was found expedient to catalyze the reaction with added sulfurized triisobutylene. This served to decrease the viscosity of the sulfur, provide better surface contact between olefin and sulfur, and measurably increased the rate of reaction. In addition, the catalyzed reaction gave little or no tarry residue.

Preparation of 4-neopentyl-5-t-butyl-1,2-dithiole-3-thione. Catalyzed reaction. In a typical experiment 1280 g. of sulfur (40 moles) and 600 g. of sulfurized triisobutylene (from a previous run) were placed in a four-necked 5-l. flask fitted with an efficient condenser, a water-cooled stirrer, a thermometer, and a dropping funnel. A Wet Test Meter containing water saturated with hydrogen sulfide was connected to the condenser. With the flask contents heated at 200–215°, 1344 g. (8 moles) of triisobutylene was added dropwise in 7.5 hr. Reaction was continued at 200° for 9 hr. and a total of 16.4 moles of hydrogen sulfide was evolved. The crude product was then vacuum distilled and the fraction (2476 g., 93% based on sulfur) boiling in the range 140–165° at 1–3 mm. was collected. The product contained 36.5% S and had a molecular weight of 255. Fractionation of 100 g. through a Piros-Glover spinning band column gave 75 g. of oil, b.p. 152° at 1 mm. An additional 10 g., b.p. 157–159° at 1.3 mm., was obtained and was identical with the main fraction except for a small shoulder at 9.92 μ in the infrared. Physical properties measured include d_4^{20} 1.18 and n_D^{20} 1.6478.

Anal. Calcd. for $C_{12}H_{20}S_3$: C, 55.33; H, 7.74; S, 36.93; mol. wt., 260. Found: C, 55.14; H, 7.79; S, 36.74; mol. wt., 265.

Uncatalyzed reaction. From 160 g. of sulfur and 168 g. of triisobutylene, treated as in the preceeding example except that 8.5 hr. reaction time was used after addition of the triisobutylene, there was obtained 147 g. (55%) of red oil, b.p. 155–185° at 1–3 mm.

Anal. Calcd. for $C_{12}H_{20}S_3$: S, 36.93; mol. wt., 260. Found: S, 36.50; mol. wt., 255.

Methyl iodide adduct of I. A solution of 3.0 g. of I in 20 g. of methanol mixed with 3.0 g. of methyl iodide gave yellow crystals on standing. Recrystallization from methanol gave pale yellow crystals, m.p. 159–161°.

Anal. Calcd. for $C_{13}H_{23}S_3I$: S, 23.90; I, 31.54. Found: S, 22.59; I, 31.50.

Metal complexes. Mercuric chloride complex. To a solution of 12 g. of I in 30 ml. of acetone there was added 14 g. of mercuric chloride in 200 ml. of acetone. After stirring 5 min. a heavy yellow precipitate formed. The precipitate was filtered, washed with hot acetone, and dried in a desiccator; yield, 20.5 g., m.p. 218–221 dec.

Anal. Calcd. for $C_{12}H_{20}S_3HgCl_2$: S, 18.08; Hg, 37.71. Found: S, 17.89; Hg, 39.00.

Cadmium iodide complex. The addition of 3.3 g. of cadmium iodide in 100 ml. of isopropyl alcohol to a solution of 5.2 g. of I in 100 ml. of isopropyl alcohol gave 6.7 g. of a yellow precipitate. The precipitate was filtered, washed with solvent and dried, m.p. 145–148°.

Anal. Calcd. for $(C_{12}H_{20}S_3)_2CdI_2$: S, 21.68; Cd, 12.68. Found: S, 21.10; Cd, 12.2.

A number of other complexes have been prepared including $ZnCl_2 \cdot C_{12}H_{20}S_3$, m.p. 189–194°; $PtCl_4 \cdot 2C_{12}H_{20}S_3$, m.p. 168–171°; and $AgNO_3 \cdot 2C_{12}H_{20}S_3$, m.p. 145–149°.

Preparation of II. Chlorination of 25 g. of I in 100 ml. of carbon tetrachloride maintaining the temperature at 30° by external cooling gave 25.5 g. of a light yellow solid, m.p. 149–151°. Recrystallization from absolute alcohol raised the m.p. to 151–152°.

Anal. Calcd. for $C_{12}H_{20}S_2Cl_2$: S, 21.42; Cl, 23.70. Found: S, 22.1; Cl, 24.7.

Preparation of 4-neopentyl-5-t-butyl-1,2-dithiole-3-one, III. The hydrolysis of the dichloro compound II was accomplished by merely refluxing 200 g. of II with 2000 ml. of water for 32 hr. After discarding the acidic water layer the red residual oil was vacuum distilled collecting 92.5 g. of III, b.p. 132–135° at 0.6–0.8 mm.

Anal. Calcd. for $C_{12}H_{20}S_2O$: C, 58.98; H, 8.24; S, 26.23. Found: C, 59.13; H, 8.03; S, 26.06.

Alcoholic hydrolysis of I. In a 4-l. flask there was placed 260 g. of I, 1200 ml. of 20% potassium hydroxide and 1200 ml. of 95% ethanol. This mixture was refluxed for 40 hr. and then carefully acidified with concd. sulfuric acid keeping the temperature below 50°. Copious amounts of hydrogen sulfide were liberated on acidification and a small amount of sulfur was isolated by filtration. The acidified solution was separated and extracted with 1 l. of ether and the ether solution evaporated on a water bath at 60°. The residue, 140 g., was fractionated and gave two major acidic fractions: A, b.p. 149–152°, 36.2 g.; B, b.p. 179–185°, 30.5 g.

A was identified as trimethyl acetic acid by conversion first to the acid chloride, b.p. 135–140°, using thionyl chloride, and then to the anilide by refluxing with aniline, m.p. 131°, reported m.p. 129° for trimethylacetanilide.

Anal. Calcd. for $C_{11}H_{15}ON$: N, 7.91. Found: N, 7.86.

The *p*-bromophenacyl ester of A (from 95% ethanol) melted at 75–76°, reported m.p. 76°.

Anal. Calcd. for $C_{12}H_{15}O_3Br$: Br, 27.83. Found: Br, 27.78.

B was identified as 4,4-dimethylvaleric acid by conversion to the amide and the anilide. B was refluxed with thionyl chloride and the acid chloride distilled. A solution of 5 g. of aniline in 50 ml. of benzene was added to 5 g. of the acid chloride, the solution refluxed 30 min., washed with water, 10% hydrochloric acid and 10% sodium hydroxide, and finally concentrated to 20 ml. total volume. White crystals separated from solution and were recrystallized from ethanol, m.p. 141–142°. The reported melting point for 4,4-dimethylvaleranilide is 141°.

Anal. Calcd. for $C_{13}H_{19}ON$: N, 6.82. Found: N, 6.83.

Conversion of the acid chloride of B to the amide with cold concd. ammonia gave white platelets, recrystallized from water, m.p. 139–141°; reported m.p. 140–141° for 4,4-dimethylvaleramide.

Anal. Calcd. for $C_7H_{15}ON$: N, 10.85. Found: N, 10.30.

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[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, COLLEGE OF ENGINEERING, UNIVERSITY OF OSAKA PREFECTURE]

Organic Polysulfides. II.[1] Polymorphism in Dibenzhydryl Tetrasulfide

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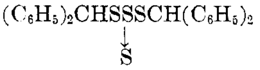
Received March 11, 1960

Two polymorphs of dibenzhydryl tetrasulfide were found. Observations of mutual convertibility and of their melting behaviors and determinations of ultraviolet and infrared absorption spectra support the conclusion that the two forms are rotational isomers in the solid state.

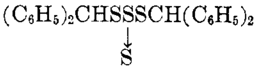
Synthesis of a series of dibenzhydryl polysulfides from mono- to hexasulfide was reported in the previous paper,[1] in which the sulfur-sulfur linkages in these polysulfides were linear. Dibenzhydryl tetrasulfide had been prepared[2] by condensation of two moles of the thiol with sulfur monochloride in carbon disulfide solution. The condensation reaction was exothermic. When all the procedures were carried out at temperatures below 30° by cooling, white pillars (I) were obtained. On the other hand, when the reaction temperature exceeded 30°, a mixture of white pillars and pale yellow needles (II) was obtained. The higher the temperatures, the greater was the proportion of yellow needles. Recrystallization of a mixture of pillars and needles from a solvent mixture of ether-petroleum ether led to an increase in the proportion of II. After two recrystallizations the white pillars disappeared completely and all the crystals were composed of the yellow needles (II). Such polymorphism was not found in other polysulfides previously reported,[1] *e.g.*, dibenzhydryl tri- and tetrasulfides and dibenzyl tri-, tetra-, and pentasulfides.

The ultraviolet absorption spectrum and molar refraction of benzhydryl tetrasulfide II were reported in the previous paper.[1] The spectrum of I overlapped with that of II within the experimental error. As II had[1] linear sulfur–sulfur linkages, by analogy, I would be expected to have the same sulfur linkages as II. Isomers such as III, IV and V are unlikely for the structure of I, as such a structure should have a different ultraviolet absorption spectrum from that of the linear one. Moreover, if the polymorphism resulted from such branched type isomers, the other polysulfides should have similar polymorphs. As stated above, such polymorphism could not be found in the other polysulfides.



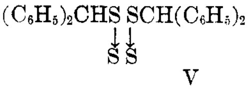
$$(C_6H_5)_2CH\underset{\overset{\downarrow}{S}}{S}SSCH(C_6H_5)_2$$

III



$$(C_6H_5)_2CHS\underset{\overset{\downarrow}{S}}{S}SCH(C_6H_5)_2$$

IV



$$(C_6H_5)_2CH\underset{\overset{\downarrow}{S}}{S}\ \underset{\overset{\downarrow}{S}}{S}CH(C_6H_5)_2$$

V

The remaining possibilities are either that these polymorphs are rotational isomers of each other (possibility A) or that molecules having the same configuration aggregate to different crystal structures I and II (possibility B). In order to decide whether the polymorphism of dibenzhydryl tetrasulfide can be ascribed to possibility A or B, mutual

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[1] Part I. J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **24**, 807 (1959).

[2] J. Tsurugi and T. Nakabayashi, *Nippon Kagaku Zasshi*, **77**, 583 (1956).