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Thiocarbonyls. VI. Studies in the Indanone and Tetralone Series[1]

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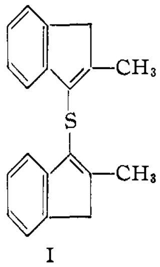
Trimeric thiones have been obtained from 1-indanone, 3-methyl-1-indanone, 1-tetralone and 3-methyl-1-tetralone. Monomeric 3-methyl-1-indanethione was obtained as a purple oil, and 3-phenyl-1-indanethione as brilliant violet crystals, unstable in air. 4-Methyl-1-tetralinthione was obtained in purple solution, from which the mercuric chloride addition compound could be isolated. 2-Phenyl-1-indanone did not react with hydrogen sulfide in cold acidic ethanol. 2-Methyl-1-indanone and 2-methyl-1-tetralone reacted with hydrogen sulfide in cold acidic ethanol to produce the α,β-unsaturated sulfides, bis-2-methyl-3-indenyl sulfide (I) and bis-2-methyl-3,4-dihydro-1-naphthyl sulfide (II), and with thiophenol in cold acidic ethanol to produce the α,β-unsaturated sulfides, phenyl 2-methyl-3-indenyl sulfide (III) and phenyl 2-methyl-3,4-dihydro-1-naphthyl sulfide (IV).

Few cyclic ketones have been converted into their thio analogs.[3] Fromm[4] reported that cyclopentanone and cyclohexanone readily form their corresponding trimeric thiones. The preparations of monomeric thiocamphor and thiomenthone have been reported by Ray[5] and Speranski.[6] Dimeric thiofluorenone was synthesized first by Bergmann and Hervey[7] and later by Campaigne and Reid[8] who were able to isolate the monomer as well as the dimer. In the light of these investigations it would seem probable that 1-indanone, 1-tetralone and substituted 1-indanones and 1-tetralones would likewise yield thio derivatives. Since steric effects are apparently important in determining whether a ketone will form a mono-, di- or trimeric thione derivative, the effect of ring substituents on the preparation of trimerized 1-indanethione and 1-tetralinthiones was studied. The compounds chosen for the investigation were the x-methyl- and x-phenyl-1-indanones, (x = 2 or 3) and the y-methyl-1-tetralones (y = 2, 3 or 4). These substituted indanones and tetralones were all mixtures of *dl*-isomers which were not separated.

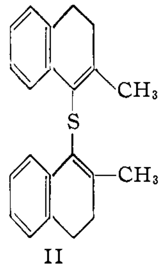
The various ketones were treated with hydrogen sulfide in cold acidic ethanol. The solutions usually became intensely purple colored, characteristic of alkyl aryl thiones,[3] but the color would gradually fade as white crystals of the trimeric thiones were deposited. In this way the trimers of 1-indanethione, 3-methyl-1-indanethione, 1-tetralinthione and 3-methyl-1-tetralinthione were obtained. The yields were always better in the indanone series, and substitution of a methyl group in the 3-position of the saturated ring improved the yields in both series. The trimers are undoubtedly complex mixtures of stereoisomers.

Monomeric thiones were isolated in three instances. By using less acidic alcohol solution, 3-methyl-1-indanethione was obtained as an unstable, high-boiling purple oil. The monomeric 3-phenyl-1-indanethione was obtained as brilliant violet crystals which gradually faded on exposure to air. This compound could not be induced to trimerize, but was oxidized by air to a light yellow solid which was a trisulfide, such as is obtained on similar treatment of thiofluorenone and thiobenzophenone.[9] A deep purple solution of 4-methyl-1-tetralinthione was obtained, but could not be isolated satisfactorily. A mercuric chloride addition product which analyzed correctly for the monomeric thione was precipitated from ether. Here again, efforts to induce trimerization were unrewarded. It is remarkable that a methyl group so far removed from the thiocarbonyl group should inhibit trimerization.

Substitution in the 2-position of both 1-indanone and 1-tetralone prevented the formation of thiones. When 2-phenyl-1-indanone was treated with hydrogen sulfide in cold solutions, using various acid concentrations, and various solvents, it was recovered unchanged. At no time was a characteristic thione color observed in the reaction mixtures. The white, crystalline products obtained by treating 2-methyl-1-indanone and 2-methyl-1-tetralone with hydrogen sulfide in cold acidic alcohol both melted nearly one hundred degrees lower than expected for the trithiones, although the initial color of the reaction mixtures indicated monomeric thiones had been formed. Analyses and molecular weight determinations indicated these compounds were bis-2-methyl-3-indenyl sulfide (I) and bis-2-methyl-3,4-dihydro-2-naphthyl sulfide (II), respectively.

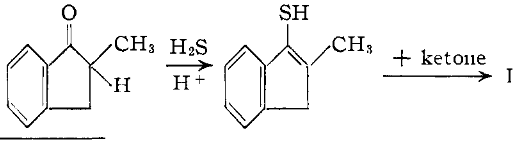


I



II

These compounds must have been formed by the reaction of hydrogen sulfide with the ketone to form the α,β-unsaturated thiol, which in turn added to another molecule of the ketone to form the unsaturated sulfide.



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[1] Taken in part from the thesis submitted by R.D.M. in partial fulfillment of the requirements for the degree Doctor of Philosophy at Indiana University, August, 1951.

[2] Frederick Gardner Cottrell Fellow in Chemistry, 1949–1951.

[3] E. Campaigne, *Chem. Revs.*, **39**, 31 (1946).

[4] E. Fromm, *Ber.*, **60**, 2090 (1927).

[5] P. C. Ray, *Nature*, **134**, 1010 (1934).

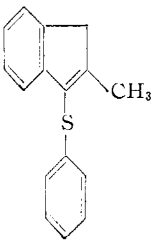
[6] N. A. Speranski, *J. Russ. Phys. Chem. Soc.*, **38**, 1288 (1906); *C. A.*, **1**, 2118 (1907).

[7] E. Bergmann and J. Hervey, *Ber.*, **62B**, 893 (1929).

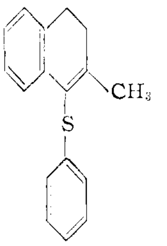
[8] E. Campaigne and W. B. Reid, THIS JOURNAL, **68**, 769 (1946).

[9] E. Campaigne and W. B. Reid, *J. Org. Chem.*, **12**, 807 (1947).

Since the expected product of the reaction of a thiol with a ketone is a mercaptal, the reaction diagrammed above seemed anomalous. To check this point, 2-methyl-1-indanone and 2-methyl-1-tetralone were allowed to react with thiophenol in acidic ethanol. In each case, a nearly quantitative yield of the α,β-unsaturated sulfides, phenyl 2-methyl-3-indenyl sulfide (III) and phenyl 2-methyl-3,4-dihydro-1-naphthyl sulfide (IV), were obtained, rather than the mercaptals.



III



IV

The infrared spectra of the two symmetrical unsaturated sulfides (I and II) as well as of the two phenylmercapto derivatives (III and IV) show absorption maxima at 7.1 μ whereas this peak is missing in spectra of trimeric 3-methyl-1-indanethione and trimeric 3-methyl-1-tetralinthione. This peak, present in the spectrum of indene but absent in the indane spectrum, has been assigned to this type of carbon-to-carbon double bond.[10]

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Experimental

Trimeric 1-Indanethione.—A solution of 5 g. (0.044 mole) of 1-indanone (m.p. 40–42°) in 250 ml. of 95% ethanol was cooled to −10° in a 500-ml. 3-necked flask in an ice–salt-bath. Hydrogen sulfide and hydrogen chloride gases were passed into the solution at rates of 2.75 and 0.75 mole per hour, respectively, for a period of 12 hours, maintaining the temperature between −10 and −12°. At the end of three hours a purple color had developed but by the end of the reaction time this color had faded and a slurry of white crystals had formed. These crystals weighed 2.6 g. (46%) and melted at 215–217°. After recrystallizing a sample three times from Cellosolve, white crystals were obtained which melted at 236–237° dec.

Anal. Calcd. for $C_{27}H_{24}S_3$: S, 21.63; mol. wt., 444. Found: S, 21.42[11]; mol. wt. (cry. in benzene), 453.

3-Methyl-1-indanethione.—Dry hydrogen chloride was passed into 50 ml. of absolute ethanol until approximately 17 g. had been absorbed. The solution was then cooled to −10 to −12° and hydrogen sulfide passed through for 30 minutes. A solution of 9.0 g. (0.061 mole) of 3-methyl-1-indanone (b.p. 127–132° at 14 mm., prepared by the method of Koelsch, Hochmann and LeClaire[12]) in 10 ml. of ethanol was then added dropwise to the well-stirred solution during the course of one hour, the hydrogen sulfide influx being continued during this addition and for 45 minutes thereafter. The temperature was maintained at −10 to −12° throughout the entire period. The purple solution was distilled in a carbon dioxide atmosphere at reduced pressure. After the forerun of alcohol, 2.3 g. of unchanged ketone, boiling at 102–104° (3 mm.), and finally a purple oil boiling at 110–112° (3 mm.) was collected. The yield of the thione was 4.6 g. (51%).

Anal. Calcd. for $C_{10}H_{10}S$: mol. wt., 162. Found: mol. wt. (cry. in benzene), 169.

The Mercuric Chloride Derivative of 3-Methyl-1-indanethione.—To 0.4 g. (0.0025 mole) of the pure 3-methyl-1-indanethione dissolved in 10 ml. of dry ether was added 100 ml. of a saturated solution of mercuric chloride in dry ether. An immediate white precipitate formed which was removed by filtration, washed with 50 ml. of ether and dried in air. The precipitate weighed 0.98 g. (92%) and did not melt up to 300°. This white material darkened on exposure to light.

Anal.[13] Calcd. for $C_{10}H_{10}SHgCl_2$: HgS, 53.64. Found: HgS, 53.95.

Trimeric 3-Methyl-1-indanethione.—The procedure used for the following preparation is similar to that suggested by Douglass[14] for the preparation of certain substituted trithianes. Dry hydrogen chloride was passed into 50 ml. of absolute alcohol until approximately 34 g. had been absorbed. The temperature was lowered to −10 to −12° and hydrogen sulfide was passed into the mixture for 15 to 30 minutes. A solution of 9 g. (0.061 mole) of 3-methyl-1-indanone in 10 ml. of alcohol was then added dropwise to the well-stirred solution over a period of 1.5 hours while continuing the flow of hydrogen sulfide. The flow of hydrogen sulfide and stirring were continued for approximately 30 minutes after the last of the carbonyl compound was added. The temperature was kept at −10 to −12° during the entire period. Upon adding the first drop of 3-methyl-1-indanone, the solution turned purple. After a short while, white crystals began to separate and by the end of the reaction a thin slurry had formed. The white product was filtered off and washed with cold alcohol. After standing overnight the mother liquor deposited additional crystals increasing the crude yield to a total of 7.0 g. (70%). Three recrystallizations from Cellosolve gave white crystals melting at 209.5–210° dec.

Anal. Calcd. for $C_{30}H_{30}S_3$: S, 19.76; mol. wt., 487. Found: S, 19.65; mol. wt. (cry. in benzene), 481.

Bis-2-methyl-3-indenyl Sulfide (I).—2-Methyl-1-indanone was prepared from α-methylhydrocinnamoyl chloride in 72% yield.[15] When 9 g. (0.061 mole) of this compound was added dropwise in ethanol solution to cold acidic ethanolic hydrogen sulfide, as previously described, the solution turned reddish-purple, and shortly deposited a slurry of white crystals. These were collected, washed with cold ethanol, recrystallized from ethanol and dried *in vacuo*. They weighed 5.2 g. (56%) and melted at 130–131.5°.

Anal. Calcd. for $C_{20}H_{18}S$: S, 11.04; mol. wt., 290. Found: S, 11.20; mol. wt. (cry. in benzene), 295.

Phenyl 2-methyl-3-indenyl Sulfide (III).—In a 125-ml. erlenmeyer flask was placed 6.6 g. (0.045 mole) of 2-methyl-1-indanone, 60 ml. of absolute ethanol and 5.0 g. (0.045 mole) of thiophenol. The solution was cooled in an ice-bath and anhydrous hydrogen chloride introduced until the solution was saturated. At this point white crystals appeared. These were filtered and dried, to give 9.5 g. (89%) of III, which melted at 79–81°. After repeated recrystallizations from ethanol and ligroin (b.p. 30–60°), this compound melted at 79–80.5°.

Anal. Calcd. for $C_{16}H_{14}S$: S, 13.44; mol. wt., 238. Found: S, 13.34; mol. wt. (cry. in benzene), 230.

3-Phenyl-1-indanethione.—A solution of 7 g. (0.034 mole) of 3-phenyl-1-indanone (m.p. 76–77°, prepared by the method of Koelsch, Hochmann and LeClaire[12]) dissolved in 50 ml. of absolute alcohol was added dropwise to the cold ethanolic acidic hydrogen sulfide solution as previously described. At the end of three hours a slurry of purple crystals was present. These were filtered, washed thoroughly with cold alcohol and dried under reduced pressure in a vaccum desiccator in an atmosphere of carbon dioxide. The yield of purple crystals which melted at 84–86.5° was 4.2 g. (59%). Three recrystallizations from alcohol raised the melting point of the compound to 89–90°.

Anal. Calcd. for $C_{15}H_{12}S$: S, 14.30; mol wt., 224. Found: S, 14.41; mol. wt. (cry. in benzene), 202.

Repeated trituration of 3-phenyl-1-indanethione in acidic

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[10] M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1950.

[11] Sulfur Analyses by Clark Microanalytical Laboratory.

[12] C. F. Koelsch, H. Hochmann and C. D. LeClaire, THIS JOURNAL, **65**, 59 (1943).

[13] R. L. Shriner, "Quantitative Analysis of Organic Compounds," 3rd ed., Edward Brothers, Inc., Ann Arbor, Mich., 1941, p. 23.

[14] I. B. Douglass, THIS JOURNAL, **73**, 3507 (1951).

[15] F. S. Kipping and G. Clarke, *J. Chem. Soc.*, **83**, 913 (1903).

alcohol failed to induce trimerization. The purple color gradually faded on exposure to air. When a 3-g. sample was dissolved in ethanol and air bubbled through it for 24 hours, a yellow precipitate was obtained, which melted at 88–91° after three recrystallizations from ethanol. This compound is apparently the cyclic trisulfide.

Anal. Calcd. for $C_{30}H_{24}S_3$: S, 20.01. Found: S, 20.22.

Attempted Preparation of Trimeric 2-Phenyl-1-indanethione.—In a 500-ml. flask 6.0 g. (0.029 mole) of 2-phenyl-1-indanone (m.p. 74–76°, prepared by aluminum chloride ring closure of α,β-diphenylpropionyl chloride) was dissolved in 300 ml. of absolute alcohol and the solution cooled to −10°. Hydrogen sulfide and hydrogen chloride were introduced at rates of 2.75 and 0.75 moles per hour, respectively, for a period of six hours. At no time did the characteristic deep-purple color of a thione appear. The solution was allowed to stand in the refrigerator for 24 hours, and then concentrated under reduced pressure. A total of 5.7 g. of crystals was obtained which melted at 71–74°. Mixed melting point with 2-phenyl-1-indanone showed them to represent a 95% recovery of the starting material. This experiment was repeated using Cellosolve as a solvent, with the same result.

Trimeric 1-Tetralinthione.—Absolute alcohol (50 ml.), cooled in an ice–methanol bath to −10 to −12° was saturated with hydrogen chloride and hydrogen sulfide gases. A solution of 7 g. (0.048 mole) of 1-tetralone (b.p. 105–107° at 2 mm., prepared by ring closure of α-phenylbutyric acid with 80% sulfuric acid) dissolved in 10 ml. of alcohol was introduced dropwise during the course of 1.5 hours, maintaining the temperature at −10 to −12° and continuing the influx of hydrogen sulfide throughout this addition and for three hours thereafter. The purple solution was stoppered and allowed to stand overnight in the refrigerator. The 1.6 g. of white crystals which appeared on standing were filtered, washed with alcohol and dried. They melted at 181–193°. Repeated recrystallizations from Cellosolve yielded 0.6 g. (7.7%) of 1-tetralinthione trimer melting at 210–211.5° dec.

Anal. Calcd. for $C_{30}H_{30}S_3$: S, 19.77; mol. wt., 487. Found: S, 19.73; mol. wt. (cry. in benzene), 496.

Trimeric 3-Methyl-1-tetralinthione.—A solution of 10 g. (0.062 mole) of 3-methyl-1-tetralone (b.p. 101–104°, prepared by the method of Tishler, Fieser and Wendler[16]) in 12 ml. of alcohol was added dropwise to the well-stirred cold hydrogen sulfide–hydrogen chloride solution over a period of 1.5 hours while continuing the flow of hydrogen sulfide. The flow of hydrogen sulfide and the stirring were continued for four hours after the addition of the last of the carbonyl compound, while temperature was kept at −10 to −12° during the entire period. A small amount of white powder which had formed was filtered, washed with alcohol and dried. The yield of the crude material melting at 222–226° was 2.0 g. Two recrystallizations from Cellosolve yielded 1.7 g. (16%) of white crystals melting at 226–227.5° dec.

Anal. Calcd. for $C_{33}H_{36}S_3$: S, 18.19; mol. wt., 528. Found: S, 18.47; mol. wt. (cry. in benzene), 513.

Mercuric Chloride Derivative of 4-Methyl-1-tetralinthione.—Fifty ml. of absolute alcohol cooled to −10 to −12° in an ice–methanol-bath was saturated with hydrogen chloride and hydrogen sulfide. A solution of 10 g. (0.062 mole) of 4-methyl-1-tetralone (b.p. 110–112° at 1 mm., prepared by the method of Kloetzel[17]) in 12 ml. of alcohol was added dropwise to the well-stirred solution over a period of 1.5 hours while continuing the flow of hydrogen sulfide. The flow of hydrogen sulfide and the stirring were continued for two hours after the addition of the last of the ketone, while temperature was kept at −10 to −12° during the entire period. The purple solution was poured into 300 ml. of ice-water and extracted with ether, and the ether solution dried over anhydrous sodium sulfate, decanted from the drying agent and poured into 200 ml. of absolute ether which had been saturated with mercuric chloride. A white precipitate which appeared was filtered, washed with absolute ether and dried in air. The precipitate weighed 12.3 g. (44%) and did not melt below 300°. This white material darkened on exposure to air.

Anal. Calcd. for $C_{11}H_{11}SHgCl_2$: HgS, 52.08. Found: HgS, 52.68.

4-Methyl-1-tetralinthione was not isolated in crystalline form. The intractable oil obtained by evaporating the purple ether solution could not be induced to crystallize nor trimerize.

Bis-(2-methyl-3,4-dihydro-1-naphthyl) Sulfide (II).—Hydrogen sulfide was passed into 50 ml. of a cold saturated solution of hydrogen chloride in ethanol for 30 minutes. A solution of 7 g. (0.044 mole) of 2-methyl-1-tetralone (b.p. 137–140° at 16 mm., prepared by the method of Tishler, Fieser and Wendler[16]) in 10 ml. of alcohol was added dropwise to the well-stirred solution over a period of 1.5 hours while continuing the flow of hydrogen sulfide. While the temperature was kept at −10 to −12°, the flow of hydrogen sulfide and the stirring were continued for approximately three hours after the last of the ketone was added. The solution immediately turned a reddish-purple, but finally a slurry of white crystals appeared. The white product was filtered off, washed with cold alcohol and dried. The crude material melted at 113–114.5°. After two recrystallizations this compound (2.9 g., 41%) melted at 114.5–115°.

Anal. Calcd. for $C_{22}H_{26}S$: S, 10.07; mol. wt., 323. Found: S, 10.02; mol. wt. (cry. in benzene), 326.

Phenyl 2-Methyl-3,4-dihydro-1-naphthyl Sulfide (IV).—In a 125-ml. erlenmeyer flask was placed 7.2 g. (0.045 mole of 2-methyl-1-tetralone, 60 ml. of absolute ethanol and 5.0 g. (0.045 mole) of thiophenol. The solution was cooled in an ice-bath and anhydrous hydrogen chloride introduced until the solution was saturated. The solution was then allowed to stand at room temperature for two hours, until a slurry of white crystals appeared. These were filtered and dried, giving 10.2 g. (90%) of crystals which melted at 49–52°. After repeated recrystallizations from ethanol and ligroin (b.p. 30–60°), this compound melted at 49–50°.

Anal. Calcd. for $C_{17}H_{16}S$: S, 12.70; mol. wt., 252. Found: S, 12.71; mol. wt. (cry. in benzene), 254.

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[16] M. Tishler, L. F. Fieser and N. L. Wendler, THIS JOURNAL, **62**, 2866 (1940).

[17] M. C. Kloetzel, *ibid.*, **62**, 1708 (1940).