bromide solution (450 cc.), the reaction flask was cooled by an ice–salt mixture. When addition was ended, the mixture was allowed to stand at room temperature for seventeen hours and then warmed by a hot plate for one hour. After hydrolysis by dilute hydrochloric acid, the mixture was worked up in the customary manner The following products were obtained: 52.5% of chlorobenzene, 60.2% of diphenyl sulfoxide, 4.1% of diphenyl sulfide, 6.4% of diphenyl, but no benzenesulfinic acid.

Summary

The chief products obtained from the reaction between arylsulfohalides and organomagnesium halides are sulfones, sulfinic acids and RX compounds having the R-group of the RMgX compound and the halogen of the sulfohalide. Previous explanations of this reaction have been corrected and a new interpretation of the reaction has been proposed.

AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE STANDARD OIL COMPANY OF INDIANA]

TETRAMETHYLETHYLENE SULFIDE

BY MERRILL A. YOUTZ AND PHILIP P. PERKINS

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It is only in comparatively recent years that substances of the type of ethylene sulfide $\overline{CH_2SC}H_2$ have been synthesized. Previous attempts to do so by treating alkylene dibromides with potassium sulfide, etc., have given either a dimer, such as diethylene disulfide or amorphous substances of even higher molecular weights. This is not especially surprising and probably in some cases long chains could be produced by the reaction of each mole of potassium sulfide with two different molecules of $C_2H_4Br_2$. However, the matter is even more involved than this as the recent successful preparation of several of these compounds by Delépine[1] has shown that, even if pure, they polymerize readily. The tendency to polymerize diminishes with increasing molecular weight. His method was to treat a 1,2-dibromide with potassium or ammonium thiocyanate, purify the dithiocyanate and to treat this with dilute sodium sulfide. Especially with the lowest member it was necessary to have the sodium hydrogen sulfide present with the sodium sulfide in order to avoid polymerization during the reaction.

The compounds are readily polymerized by bases or acetic or sulfuric acids. Nitric acid oxidizes them to sulfuric or sulfonic acids. Hydrochloric acid appears to combine forming a chloromercaptan which can be removed with sodium plumbite, etc. Probably the oxidation by nitric

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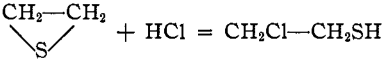
[1] Delépine, *Compt. rend.*, **171**, 36 (1920); **172**, 158 (1921); *Bull. soc. chim.*, [4] **27**, 740 (1920); **29**, 136 (1921).

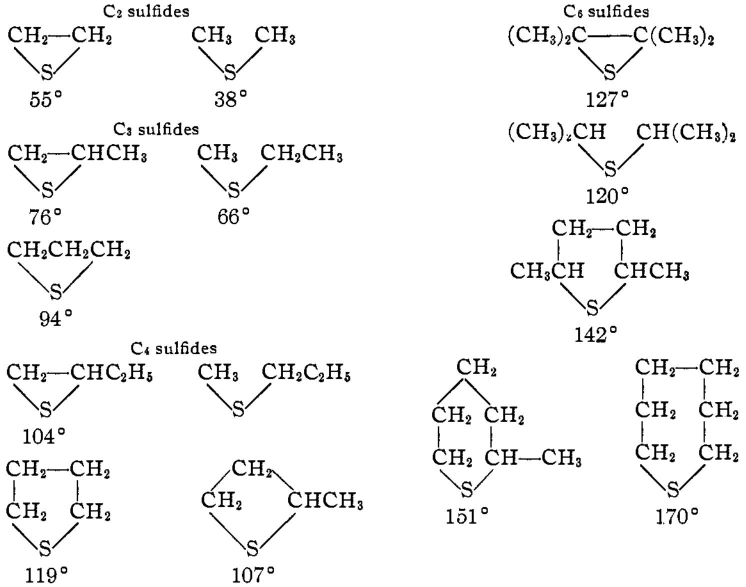
acid, which takes the same course as with a mercaptan, is preceded by this mercaptan formation



They form addition compounds with heavy metal salts and methyl iodide. The boiling points are a little higher than those of the corresponding alkyl sulfides but lower than those of the isomers having a larger ring.

TABLE I

SULFIDES AND THEIR BOILING POINTS



The tetramethylethylene sulfide here described resembles the simpler members in its chemical properties though it is more stable. It was prepared by the reactions

$$\text{Acetone} \xrightarrow{\text{H}} \text{Pinacone hydrate} \xrightarrow{70\%\ \text{HBr}} \text{Teramethylethylene dibromide} \xrightarrow{\text{KSCN}}$$

$$\text{Dithiocyanate} \xrightarrow{Na_2S} \text{Sulfide}$$

As might be expected from its symmetry, it is a solid, m. p. 76°, b. p. 127°, and has great powers of crystallization. The crystals are usually needle-like if sublimed, but if allowed to sublime at room temperature by standing in a container, it forms perfect cubic crystals of diamond-like brilliancy. On one occasion the whole of a preparation crystallized overnight from a petroleum ether solution in a single crystal over two inches long and weighing about ten grams. It has an extremely powerful odor, not exceedingly unpleasant and resembling that of camphor. It is very soluble in all the usual organic solvents though not in water. It cannot be recrystallized satisfactorily at elevated temperatures because of its volatility. It can be recrystallized from low-boiling (25–40°) petroleum ether by evaporating off part of the solvent with an air stream at a low temperature and then chilling to −15 or −20° and filtering on a cold filter. It can also be purified by sublimation.

It is easily polymerized to amorphous insoluble particles by concentrated sulfuric acid even in dilute naphtha solution, from which it is very completely removed. It forms addition compounds with mercuric chloride and with silver nitrate in absolute or 95% alcohol solution. It reacts only slightly with methyl iodide.

Experimental Part

Pinacone Hydrate.—This was made from acetone by reduction with magnesium amalgam.[2]

Tetramethylethylene Dibromide.—This was made according to the procedure of Thiele[3] by treating pinacone hydrate with 70% hydrobromic acid; yields, 50–85%. The use of spent acid resaturated with hydrogen bromide gave progressively lower yields. Apparently a liquid substance accumulates in solution in the acid. It is a severe lachrymator and is probably the bromohydrin, which is the chief product if insufficient or too weak acid is used. The crude product was dried and recrystallized from glacial acetic acid and used soon after.

Tetramethylethylene Dithiocyanate.—Fifty cc. of methyl alcohol and 19.4 g. of potassium thiocyanate (or 15.2 g. of ammonium thiocyanate, 4 moles) were refluxed for a few minutes; 12.2 g. of dibromide was added and the mixture first warmed and shaken, and then refluxed for ten to fifteen minutes; 250 cc. of water was added and the mixture extracted four times with 100-cc. portions of light petroleum ether while still slightly warm. The dithiocyanate is very insoluble in cold naphtha and only slightly soluble in warm naphtha. The naphtha was nearly all evaporated by air blowing on the steam-bath; the remainder was cooled in ice and the hard grainy precipitate filtered with suction. The yield was 4.5–5.5 g. (45–55%). Less potassium thiocyanate reduces the yield, while more increases it only slightly. The dibromide should be freshly recrystallized, dry and free from acetic acid. The dithiocyanate, recrystallized from alcohol, melts at 61°.

Anal. Calcd.: N, 14.0; S, 32.0. Found: N, 14.4, 14.5; S, 31.4, 31.7.

Tetramethylethylene Sulfide.—Twenty grams of dithiocyanate and 50 cc. of methyl alcohol were mixed in a flask provided with a reflux condenser. A solution of 25 g. of $Na_2S \cdot 9H_2O$ (calcd., 24 g.) in 50 cc. of water was added. A slight warming occurred and the mixture was heated gently (not boiled) with shaking for thirty minutes and then cooled; 50 cc. of very light petroleum ether (b. p. 20–35° or 25–35°) was poured through the condenser to dissolve out sublimed sulfide, then the mixture was placed in a separatory funnel, water added, the mixture shaken and the layers separated. The lower layer was washed again with 50 cc. of the petroleum ether. These extracts were evaporated by an air stream while keeping very cold, until nearly all the solvent was gone (6–8 cc.). The evaporation must not be prolonged as the sulfide is very volatile.

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[2] Marvel, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1925**, Vol. V, pp. 87–89.

[3] Thiele, *Ber.*, **27**, 455 (1894).

The solution was chilled in a freezing mixture, the crystals filtered with slight suction on a cold Büchner funnel with paper and the filtrate added to the next preparation; yield, 90–95%. It may contain dithiocyanate, from which it can be freed by sublimation; m. p. 76.1–76.6°; b. p. 127° (corr.) (by the Siwolliboff capillary tube method); sulfur, 27.5%; calcd., 27.6%. The molecular weight of the crude sulfide was determined by the freezing-point method in benzene: (1) 16.00 g. of solvent; 0.1423 g. of sample, depression 0.385°, molecular weight 115.5; (2) 0.2672 g. of sample, depression 0.719°, molecular weight 116.1, calcd. 116.19. Hence it contained no polymers.

Summary

Tetramethylethylene sulfide was prepared by the series of reactions acetone → pinacone hydrate → tetramethylethylene dibromide → dithiocyanate → sulfide, and some of its properties have been recorded.

WHITING, INDIANA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE STANDARD OIL COMPANY, INDIANA]

TRIMETHYL- AND TRIMETHYLETHYLTHIOPHENE

BY MERRILL A. YOUTZ AND PHILIP P. PERKINS

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Perhaps the most obvious method of preparing polyalkylthiophenes of known structure is by means of the reaction of phosphorus pentasulfide or phosphorus trisulfide on 1,4-dicarbonyl compounds. If the α-positions of the thiophene are to be substituted with alkyl groups, the carbonyl compound must be a diketone. The preparation of such compounds has proved to be extremely difficult. The only member thus far reported is 3,4-dimethylacetonylacetone prepared by Ciamician and Silber[1] by the action of light on methyl ethyl ketone and by Vladesco[2] by the action of sodium on methyl chloro-ethyl ketone. Willstätter and Clark[3] reported a large amount of work on attempts to produce such a diketone. While the action of iodine on sodium acetoacetic ester readily yields diacetylsuccinic ester, which is hydrolyzable to acetonylacetone with good yields, the attempt to carry out an analogous reaction with ethyl sodium acetoacetic ester has uniformly failed. Also the attempt to introduce alkyl groups into sodium diacetylsuccinic ester leads chiefly to ethers, and such of the desired compound as is produced readily loses one or more acetyl groups by hydrolysis or alcoholysis.[3] We have found that another variation of this synthesis gives negative results: the action of sodium on α-bromo-α-ethyl acetoacetic ester. An attempt to repeat the work of Vladesco where sodium is allowed to react with methyl chloro-ethyl ketone yielded no detectable amount of the desired diketone. Also the ethyl

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[1] Ciamician and Silber, *Ber.*, **45**, 1540 (1912).

[2] Vladesco, *Bull. soc. chim.*, [3] **6**, 809 (1891).

[3] Willstätter and Clark, *Ber.*, **47**, 291–310 (1914).