

Kohler and Barrett and in addition to the reduction produced we isolated a small quantity of another solid product. By recrystallization from 50% methyl alcohol this new product was obtained in colorless plates melting at 126°.

Anal. Calcd. for $C_{22}H_{22}O_2N$: C, 80.0; H, 6.7. Found: C, 80.0; H, 6.6.

The composition indicates the addition of C_2H_4 to the oxide, but the substance was obtained in an amount too small for further investigation.

Summary

There are two types of reaction between isoxazoline oxides and organic magnesium compounds.

In one type of reaction the organic magnesium combines at the ends of the unsaturated system $C=NO$. The extremely unstable products of this system usually undergo rearrangement to open-chained compounds which react with two more molecules of the reagent.

In another type of reaction the magnesium compounds act as reducing agents. The product of this reaction is an open-chained hydroxy oxime formed by adding two atoms of hydrogen to the oxide.

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STUDIES IN THE DIPHENYL SERIES. II. SOME ANTIMONY DERIVATIVES OF DIPHENYL

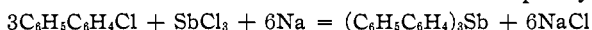
BY DAVID E. WORRALL

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The physiological activity of certain organo-metallic compounds has revived interest and attention to this great class of compounds in the past two or three decades. This has been particularly true of arsenic and in a previous communication¹ some arsenic derivatives of diphenyl were described. While the antimonials have not been as thoroughly studied, it has been found that in certain diseases of protozoan origin they are even more efficacious than arsenicals, a fact that naturally has stimulated work in this field. No work, however, has been done previously in the diphenyl series; therefore some of the more accessible antimonials containing diphenyl have been prepared in this Laboratory and their properties studied.

Tri-biphenylstibine was obtained, using the method of Michaelis and Reese,² by the action of an excess of sodium on 4-chlorodiphenyl and anti-



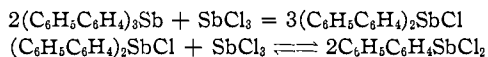
mony chloride dissolved in benzene. The yield was excellent. As in similar condensations with arsenic chloride, diphenyl was formed as a by-prod-

¹ Worrall, *THIS JOURNAL*, 52, 664 (1930).

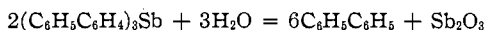
² Michaelis and Reese, *Ber.*, 15, 2877 (1882).

uct. Tri-biphenylstibine instantly decolorized bromine or permanganate solutions because of the ease with which it formed pentavalent antimony derivatives. It did not react with methyl iodide, in this respect differing from tri-biphenylarsine. The halogen addition products, tri-biphenylarsine dichloride, for example, were found to be less sensitive to water than the corresponding arsenic derivatives. In other respects the two series of compounds have similar properties, separating from chloroform solution with a molecule of chloroform, decomposing at the melting point, etc.

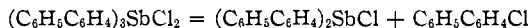
The mono- and diarylated derivatives were obtained together by long heating of antimony chloride with tri-biphenylstibine. According to Morgan and Micklethwait³ two reactions take place with triphenylstibine, the second of which is reversible. The changes would be represented as follows with tri-biphenylstibine



A fairly good yield of the mixture was obtained, but in the separation by fractional crystallization much material was lost and the amounts of pure substances obtained were much less than the theoretical. Vacuum distillation could not be used, as the substances decomposed. The amount of di-biphenylstibine chloride isolated was about one-fourth of that of mono-diphenylstibine chloride. A certain amount of hydrolysis of tri-biphenylstibine, apparently due to wet material, took place when it was heated with antimony chloride for antimonous oxide and diphenyl were isolated from the products of the reaction and identified.

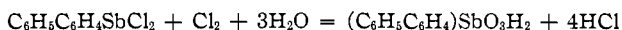


The low yield of the di-phenylstibine chloride led to a study of the effect of heat on tri-biphenylstibine dichloride in the hope that it might give the desired substance by the reaction



Such a decomposition actually took place but additional changes followed. for the quantity of desired product isolated was negligible. Considerable chlorodiphenyl was isolated.

Both mono-diphenylstibine dichloride and di-biphenylstibine chloride when hot gave off irritating vapors, but decomposed when the boiling point was attained. They are readily hydrolyzed and can be changed to stibinic acids by treating with chlorine before hydrolysis.



The intermediate tetrachloride may be isolated if desired by working with dry reagents. The stibine acids were air dried at 100° before analysis.

³ Morgan and Micklethwait, *J. Chem. Soc.*, 99, 2286 (1911).

Most of these diphenyl antimony derivatives, as was true of the corresponding arsenicals, decompose when heated; consequently, the melting points vary if the rate of heating changes and are not always easy to reproduce.

Experimental

Tri-biphenylstibine.—To a solution of 100 g. of 4-chlorodiphenyl and 40 g. of freshly distilled antimony chloride in 500 cc. of dry benzene was added an excess (50 g.) of granulated sodium. The mixture was heated under a reflux condenser until boiling started. The reaction subsequently became so vigorous that it was moderated by immersion of the container in ice water. This spontaneous action slackened in about half an hour and heat was again applied for several hours. The product was filtered while hot, the black residue twice extracted with 250 cc. of hot benzene and the combined filtrates concentrated to approximately 250 cc. On addition of an equal volume of warm alcohol the entire mass quickly became semi-solid due to the separation of a bulky crystalline precipitate. It was filtered with difficulty by suction, washed thoroughly with cold alcohol and dried at 100°; yield, 89 g.

Anal. Calcd. for $C_{36}H_{27}Sb$: Sb, 21.0. Found: Sb, 21.2.

The last filtrate was evaporated to dryness and steam distilled. The distillate contained diphenyl, identified by its odor and properties, contaminated with some 4-chlorodiphenyl. The residue was not further examined.

Tri-biphenylstibine is easily dissolved by chloroform, methyl iodide or benzene, separating from the latter in microscopic hair-like crystals. It melts at 176.5–177.5° with preliminary softening. Decomposition takes place at the boiling point with the formation of diphenyl and antimony among other things.

Tri-biphenylstibine dichloride, dibromide and di-iodide were obtained by dissolving 5 g. of tri-biphenylstibine in 20 cc. of pure dry chloroform, adding slightly less than the theoretical amount of the corresponding halogen in chloroform and filtering the resulting precipitate. This procedure gave a pure white product, not otherwise obtained. With the chloride this precaution was not necessary. The halogen in all cases was instantly absorbed plus considerable heat evolution. The products contained chloroform of crystallization and melted with preliminary softening and decomposition.

	Crystal form	M. p., °C.	Yield, g.	Analysis, ⁴ %	Calcd.	Found
Dichloride	Small prisms	273–274	5.4	Cl,	9.0	8.9
Dibromide	Narrow plates	259–260	5.6	Br,	18.6	18.4
Di-iodide	Small plates	176–178	6.0	I,	26.6	26.8

Tri-biphenylstibine Hydroxide.—The above halogen derivatives did not react with water, hot or cold, and only slowly with warm 95% ethyl alcohol. Boiling for an hour with alcohol containing ammonia, however, converted them quantitatively into tri-biphenylstibine hydroxide.

Anal. Calcd. for $C_{36}H_{27}Sb(OH)_2$: Sb, 19.8. Found: Sb, 19.6

It is sparingly soluble in hot alcohol, crystallizing out in small flat needles. It begins to sinter at 205° and melts with foaming at 210–211°. The substance is almost insoluble in benzene.

⁴ A weighed amount of the substance after heating for an hour with alcoholic ammonia was evaporated to dryness, extracted with water, and the filtered solution treated in the usual way with silver nitrate. The chloroform of crystallization escaped intact into the air.

Tri-biphenylstibine sulfide.⁵—Microscopic needles from the action of hydrogen sulfide on an alcohol solution of the hydroxide.

Anal. Calcd. for $C_{36}H_{27}SbS$: S, 5.2. Found: S, 5.3.

It softens above 168° , melting with foaming at 173° .

Action of Antimony Trichloride.—A mixture of 10 g. of tri-biphenylstibine and 8 g. of antimony in 25 cc. of xylene was heated to 220 – 240° in a sealed tube for 100 hours. The paste-like product was filtered by suction and washed with cold benzene; yield, 9.6 g. The black filtrate on examination was found to contain an appreciable amount of diphenyl.

The solid product proved to be a mixture of two substances difficult to separate and purify. It was dissolved in hot benzene and the resulting cloudy discolored solution filtered while warm. The filtrate on standing deposited crystals which were removed and the new filtrate further concentrated until a new crop of crystals formed. Each lot was dissolved in warm benzene and the process repeated a number of times. Eventually the mixture was separated into two portions, the less soluble consisting of needle-like crystals and the main part of lustrous plates. Slightly more than half a gram of di-biphenylstibine chloride together with two grams of biphenylstibine dichloride was isolated. The final substances probably contained traces of impurities due to hydrolysis, as a slightly cloudy solution formed when benzene was used as a solvent. This cloudiness could be cleared up with hydrogen chloride gas, in harmony with the fact that the chlorides are much more soluble in benzene than the corresponding oxygen derivatives.

Mono-biphenylstibine Dichloride.—Lustrous white plates from benzene melting with preliminary softening at 132 – 133° .

Anal. Calcd. for $C_{12}H_9SbCl_2$: Cl, 20.5. Found: Cl, 20.4.

The vapors from the hot substance are irritating to the throat, while the skin of the face is slightly sensitive to the solid itself.

Mono-biphenylstibine Oxide.—Obtained as a white powder from the dichloride by the action of alcoholic ammonia. It softens above 155° , melting slowly at 159 – 160° .

Anal. Calcd. for $C_{12}H_9SbO$: Sb, 41.9. Found: Sb, 42.2.

Mono-biphenylstibinic Acid.—Biphenylstibine tetrachloride was prepared from the dichloride as a thick sirup which partially crystallized on rubbing with a glass rod, by the action of chlorine in chloroform solution and subsequent evaporation of the solvent. It was converted directly by stirring with water into the stibinic acid, a white powder decomposing above 300° .

Anal. Calcd. for $C_{12}H_{11}SbO_3$: Sb, 37.5. Found: Sb, 37.9.

Di-biphenylstibine Chloride.—Obtained by the action of antimony chloride on tri-biphenylstibine.

Anal. Calcd. for $C_{24}H_{18}SbCl$: Cl, 7.6. Found: Cl, 7.8.

It is less soluble than phenylstibine dichloride, separating from benzene in aggregates of small needles. It softens gradually above 150° , melting at 187 – 188° .

This substance was also obtained by heating tri-biphenylstibine dichloride above its melting point. Foaming occurred and a perceptible odor of chloroform became evident. On further heating the vapors contained chlorodiphenyl and a substance very irritating to the nose. A good yield of 4-chlorodiphenyl was obtained, but the first-formed di-biphenylstibine chloride obviously underwent decomposition, as only traces of it were isolated.

⁵ Sulfur was determined by the method of Carius. The organic matter was not completely destroyed, but the residue after dilution with water was removed and found to be sulfur free.

Di-biphenylstibinic Oxide.—Crystalline powder, melting at 120–121° with preliminary softening, obtained from the preceding chloride by the action of alcoholic ammonia.

Anal. Calcd. for $C_{48}H_{36}Sb_2O$: Sb, 27.9. Found: Sb, 28.1.

Di-biphenylstibinic Trichloride.—Pale yellow flat needles from the action of chlorine on di-biphenylstibine chloride dissolved in chloroform. It softens above 200°, melting at 210°.

Anal. Calcd. for $C_{24}H_{18}SbCl_3$: Cl, 19.9. Found: Cl, 20.0.

Di-biphenylstibinic Acid.—White amorphous powder from the trichloride and alcoholic ammonia. It softens above 201° and melts with decomposition at 204–205°.

Anal. Calcd. for $C_{24}H_{18}SbO_2$: Sb, 26.5. Found: Sb, 26.5.

Summary

Tri-biphenylstibine has been obtained by the interaction in benzene solution of chlorodiphenyl, antimony chloride and sodium.

It is converted into a mixture of mono- and di-biphenylstibine chloride by long heating with antimony chloride. Various tri- and pentavalent antimony derivatives of these substances have been prepared.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

RESEARCHES ON CHLORIMINES. I. ORTHO-CHLOROBENZALCHLORIMINE AND ANISALCHLORIMINE

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There is evidence¹ that benzalchlorimine has been prepared, but due to its instability it has not been isolated and analyzed. Luxmoore² apparently obtained benzalchlorimine from benz-*anti*-aldoxime and phosphorus trichloride but the compound decomposed into hydrogen chloride and benzonitrile even below 0°. Later workers³ apparently obtained impure benzalchlorimine from monochloramine and benzaldehyde but the chlorimine could not be purified as it readily decomposed into hydrogen chloride and benzonitrile.

The decomposition of benzalchlorimine may be represented by the equation, $C_6H_5CH=NCl \rightarrow C_6H_5CN + HCl$. It seemed possible that by substituting electronegative groups in the phenyl radical a more stable chlorimine might result. As a first step in testing this idea, *o*-chlorobenzalchlorimine and anisalchlorimine have been prepared from the corresponding aldehyde and monochlorimine in alkaline solution. Both of these chlorimines are apparently more stable than benzalchlorimine.

¹ For evidence see Hauser, *THIS JOURNAL*, **52**, 1108 (1930).

² Luxmoore, *J. Chem. Soc.*, **69**, 191 (1896).

³ Forster, *ibid.*, **107**, 265 (1915); Raschig, "Schwefel und Stickstoffstudien," 1924, p. 78.