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 $C_{24}H_{19}SbO_2$: 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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RESEARCHES ON CHLORIMINES. I. ORTHO-CHLOROBENZALCHLORIMINE AND ANISALCHLORIMINE

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There is evidence[1] that benzalchlorimine has been prepared, but due to its instability it has not been isolated and analyzed. Luxmoore[2] apparently obtained benzalchlorimine from benz-*anti*-aldoxime and phosphorus trichloride but the compound decomposed into hydrogen chloride and benzonitrile even below 0°. Later workers[3] 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, $C_6H_5CH{=}NCl \longrightarrow C_6H_5CN + HCl$. 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 benzalchlo-

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[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.

rimine. Furthermore, *o*-chlorobenzalchlorimine is much more stable than anisalchlorimine. This might be explained by assuming an *anti* configuration[4] for the former chlorimine and a *syn* configuration for the latter. However, there seems to be evidence that they are both *anti* compounds. The analogous oximes have *anti* configurations[5] when prepared from the corresponding aldehydes and hydroxylamine in alkaline solution, and as the chlorimines were prepared by a similar method, possibly they also have *anti* configurations. Luxmoore's work[2] indicates that *syn*-benzalchlorimine is so unstable as to be incapable of existence. He found that benz-*anti*-aldoxime with phosphorus trichloride presumably yielded the *anti* chlorimine, while benz-*syn*-aldoxime was instantly converted by the same reagent into benzonitrile, which is the decomposition product of the chlorimine. Of course there is a possibility that the latter reaction was simply a dehydration. It would be interesting to repeat Luxmoore's work with *syn* and *anti* aldoximes having electronegative groups in the benzene ring.

o-Chlorobenzchlorimine and anisalchlorimine liberate hydrogen chloride slowly at room temperature and more rapidly as the temperature is raised. If *anti* configurations for these chlorimines are assumed, then either the elements of hydrogen chloride split off directly from the *anti* compounds or the *anti* modifications are first transformed into the *syn* isomers, which then decompose. A trace of hydrogen chloride might favor such a transformation.[6] The isolation of a second isomer should help to decide this.

Since *o*-chlorobenzalchlorimine is more stable than anisalchlorimine, chlorine in the ortho position appears to have a greater influence on the stability of the chlorimine than has the methoxy group in the para position. A further study of the stabilizing influences of these and other substituent groups is now in progress.

Experimental

o-Chlorobenzalchlorimine[7] and anisalchlorimine, prepared by the condensation of the corresponding aldehyde with monochloramine[1] in cold aqueous solution, were filtered and washed with cold water. Since crude *o*-chlorobenzalchlorimine melts around 20°, it is best to use a cooled funnel if the temperature of the room is above 20°. How-

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[4] By analogy with oximes and similar compounds stereoisomeric ald-chlorimines are possible. For stereoisomeric keto-chlorimines, see, Stieglitz and Peterson, *Ber.*, **43**, 782 (1910).

[5] In this discussion the generally accepted ideas of *syn* and *anti* representation are used. Brady and Bishop, however, have presented some evidence that these should be reversed. Brady and Bishop, *J. Chem. Soc.*, **127**, 1357 (1925).

[6] It is interesting to note that although keto-chlorimines could not be induced to change from one isomer to the other by artificial means, the change was effected once when one isomer was allowed to stand for some time. Peterson, *Am. Chem. J.*, **46**, 325 (1911).

[7] This chlorimine was previously obtained in an impure condition (see ref. 1).

ever, this precaution is unnecessary in the case of anisalchlorimine as its melting point is higher. A yield of approximately 85% of crude chlorimine was obtained in each case. The chlorimines were recrystallized by dissolving them in 95% alcohol at room temperature, adding just enough water so that the precipitate which formed redissolved on shaking and allowing the solution to stand in an ice-bath or cool place. Since the chlorimines slowly decompose in alcohol as described below, the crystals were filtered shortly after they were formed, pressed on a porous plate until dry and analyzed. Nitrogen was determined by the Kjeldahl method. Active chlorine was determined by treating an alcoholic solution of the chlorimine with potassium iodide solution and concentrated hydrochloric acid and immediately titrating with sodium thiosulfate.

Anal. Calcd. for $ClC_6H_4CH{=}NCl$: N, 8.05; Cl, 20.38. Found: N, 8.07, 8.13; Cl, 20.33, 20.26.

Anal. Calcd. for $CH_3OC_6H_4CH{=}NCl$: N, 8.26; Cl, 20.92. Found: N, 8.19, 8.42; Cl, 20.73, 20.84.

Slightly low results for nitrogen were obtained when anisalchlorimine, either free or in alcoholic solution, was allowed to stand for some time in concentrated hydrochloric acid and then neutralized and distilled into standard acid. Results are liable to be low for active chlorine unless the determination is carried out rapidly using well cooled solutions.

o-Chlorobenzalchlorimine, $ClC_6H_4CH{=}NCl$.—This substance was obtained as small white crystals and melted at 27–29°. By recrystallizing very slowly, small needles were obtained which melted at 28–29°. When the chlorimine was heated above its melting point, a temperature was reached at which it suddenly decomposed rather violently. This decomposition temperature ranged from 120–160°, depending upon the rate of elevation of temperature and possibly upon other factors. About 0.5 g. of one preparation in a small test-tube was immersed in a bath at 146° and the temperature gradually raised to 155°, when the chlorimine suddenly decomposed rather violently, evolving fumes of hydrogen chloride and leaving a residue from which *o*-chlorobenzonitrile was isolated. The nitrile was identified by the mixed melting point method and by hydrolysis to the corresponding acid.

o-Chlorobenzalchlorimine kept in a desiccator over solid sodium hydroxide for several hours at room temperature was shown by analysis for active chlorine to be practically unchanged. Even after five days an analysis showed that about 90% of the chlorimine remained unchanged.

The chlorimine is also quite stable in benzene solution. A benzene solution of the chlorimine was allowed to stand at room temperatures (18–24°) for fifteen days. When the benzene was allowed to evaporate, an oil was obtained which was identified as slightly impure *o*-chlorobenzalchlorimine. Recrystallization from alcohol yielded the pure chlorimine.

The chlorimine slowly decomposed in alcoholic solution yielding principally *o*-chlorobenzaldehyde. The phenylhydrazone of this aldehyde was prepared and identified by the mixed melting point method. Since alcohol was used as the crystallizing solvent, the following preliminary experiment was performed in order to determine whether the rate of decomposition of the chlorimine in alcoholic solution was appreciable. The decomposition of the chlorimine in 95% alcohol solution (approx. 0.2 *M*) at 12–18° was followed by titrating a 10-cc. portion of the solution with sodium thiosulfate immediately after the solution was prepared and then every twenty-four hours until the decomposition was complete. At the end of the first twenty-four hours the amount of thiosulfate required was practically the same as the amount required for the initial titration. At the end of forty-eight hours a slightly smaller amount of thiosulfate was required. The decomposition then proceeded more rapidly until it was practically complete after five or six days. The acidity of the solution increased as the decomposition proceeded. The increased acidity, due perhaps to the decomposition of some chlorimine or possibly some ethyl hypochlorite, apparently accelerated the rate of hydrolysis of the chlorine. A more detailed study of this will be made.

Anisalchlorimine, $CH_3OC_6H_4CH{=}NCl$.—This substance, obtained as well-formed white crystals from alcohol, melted at 43–44° when it was immersed in a bath at 40° and then heated gradually. Due perhaps to slight decomposition the chlorimine began to soften at a lower temperature when the melting point was determined in the usual way. Similarly to *o*-chlorobenzalchlorimine, when anisalchlorimine was heated above its melting point, a temperature was reached at which the substance decomposed rather violently into hydrogen chloride and the nitrile. This decomposition temperature varied from 60 to 85°. Doubtless some decomposition occurred at lower temperatures but due to the greatly increased rate of decomposition at higher temperatures the chlorimine appeared to decompose all at once. Sometimes this reaction was almost explosive in nature. When the chlorimine in a melting point tube was immersed in a bath at 69–70° over two minutes elapsed before sudden decomposition occurred. However, at 81–82° violent decomposition took place after several seconds. When a small amount of one preparation was kept at 65° for several minutes the inside of the tube became coated with a white solid. However, when a larger quantity, about 0.5 g., was immersed in a bath at 65° for several seconds, it decomposed violently, evolving hydrogen chloride and leaving a residue from which the nitrile and imine hydrochloride were isolated. Evidently the heat of decomposition of some of the chlorimine raised the temperature of the rest so that the decomposition became violent. The nitrile was identified by the mixed melting point method and by hydrolysis to the corresponding acid. The imine hydrochloride was hydrolyzed to anisaldehyde, which was identified by the preparation of the phenylhydrazone.

Anisalchlorimine decomposes at room temperature more rapidly than *o*-chlorobenzalchlorimine. After standing in a desiccator over solid sodium hydroxide for twenty-four hours, an analysis for active chlorine indicated that only 8% of the chlorimine remained unchanged. After five days the material had a mouldy appearance and an analysis showed that only a trace of active chlorine was left. When 0.873 g. of this material was warmed with several small portions of anhydrous ether and filtered, 0.346 g. remained as the insoluble portion; calculated by difference, 0.527 g. of the material was dissolved by the ether. When the ether was evaporated about 0.4 g. of residue was obtained, which after recrystallizing from ligroin was identified as anisic nitrile by the mixed melting point method and by hydrolysis to the corresponding acid. The fraction of material insoluble in ether was shown to consist almost entirely of the imine hydrochloride. The latter compound was hydrolyzed to ammonium chloride and anisaldehyde and the phenylhydrazone of the aldehyde was prepared. The decomposition of the chlorimine may therefore be represented by the equations

$$2CH_3OC_6H_4CH{=}NCl \longrightarrow 2CH_3OC_6H_4CN + 2HCl$$
$$CH_3OC_6H_4CH{=}NCl + 2HCl \longrightarrow CH_3OC_6H_4CH{=}NH{\cdot}HCl + Cl_2$$

A crude portion of the chlorimine after standing for several hours in a desiccator spontaneously decomposed rather violently, evolving fumes of hydrogen chloride and leaving a brown residue from which the nitrile was isolated.

Apparently anisalchlorimine also decomposed in benzene solution according to the above equations. After a benzene solution had stood at room temperatures (18–24°) for several days, chlorine was detected above the solution by means of starch–potassium iodide paper. After fifteen days the benzene was allowed to evaporate, and the residue obtained was shown to consist principally of the imine hydrochloride and the nitrile.

Since anisalchlorimine in alcoholic solution yielded principally anisaldehyde, apparently an hydrolysis similar to that described for *o*-chlorobenzalchlorimine occurred.

Reduction of Anisalchlorimine to *o*-Methoxybenzylamine.—Two grams of the chlorimine in alcoholic solution was reduced with sodium amalgam at about 30° by the method described in a recent paper.[1] A 64% yield of white crystals of amine hydrochloride was obtained.

Anal. Calcd. for $C_8H_{11}ON \cdot HCl$: N, 8.05. Found: N, 8.04.

Summary

o-Chlorobenzalchlorimine and anisalchlorimine were prepared from the corresponding aldehyde and monochloramine. Since the former chlorimine is more stable than the latter, chlorine in the ortho position apparently has a greater influence on the stability of the chlorimine than has the methoxy group in the para position.

The chlorimines decompose slowly at room temperatures and more rapidly as the temperature is raised into hydrogen chloride and the corresponding nitrile.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. V. PREPARATION AND RESOLUTION OF 2,4,6,2',4',6'-HEXANITRO-3,3'-DICARBOXYDIPHENYL[1]

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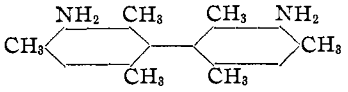
The resolution of 2,4,6,2',4',6'-hexamethyl-3,3'-diaminodiphenyl (I)[1b] (diaminodimesityl) demonstrated that the groups in the 2,6,2',6'-positions in diphenyl could all be methyl and still render the molecule capable of existing in optically active forms. The conclusion from this research was that probably any group in place of the methyl would be equally satisfactory for producing similar results providing it is sufficiently large.

In this investigation the preparation of a compound containing four nitro groups in the 2,2',6,6'-positions was undertaken and the specific compound studied was 2,4,6,2',4',6'-hexanitro-3,3'-dicarboxydiphenyl (II).



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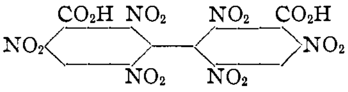

II

This substance is of particular interest as compared to diaminodimesityl because of the entirely different electrochemical character of the nitro

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[1] Previous papers in this field are: (a) Hyde and Adams, THIS JOURNAL, **50**, 2499 (1928); (b) Moyer and Adams, *ibid.*, **51**, 630 (1929); (c) Stanley and Adams, *Rec. trav. chim.*, **48**, 1035 (1929); (d) THIS JOURNAL, **52**, 1200 (1930).

[2] This communication is an abstract of portions of theses submitted by W. W. Moyer and L. H. Bock in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.