[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

THE ACTION OF AROMATIC GRIGNARD REAGENTS ON ARYLARSINE OXIDES[1]

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The preparation of several tetra-arylarsyl oxides from arsenic trioxide and arylmagnesium halides has been described recently and a reaction mechanism to account for their formation has been suggested.[3]

A second method for the preparation of tetra-arylarsyl oxides, by means of which simple as well as mixed oxides of the type RR'As—O—AsR'R can be obtained, is the subject of this paper.

Diphenyl, di-*p*-tolyl, di-*p*-anisyl and di-α-naphthyl mercury were prepared by the interaction of arylmagnesium halides and mercuric chloride. $RMgX + HgCl_2 \longrightarrow RHgX + ClMgX$; $RHgX + RMgX \longrightarrow RHgR + MgX_2$. Hitherto only diphenylmercury has been obtained by this method.[4]

The diarylmercury compounds were heated with arsenic trichloride with the formation of aryldichloro-arsines which, upon hydrolysis, yielded arylarsine oxides.

$$\begin{aligned} RHgR + AsCl_3 &\longrightarrow RAsCl_2 + ClHgR \\ ClHgR + AsCl_3 &\longrightarrow RAsCl_2 + HgCl_2 \\ RAsCl_2 + 2NaOH &\longrightarrow RAsO + 2NaCl + H_2O \end{aligned}$$

In those instances in which it is impractical to prepare the mercury diaryls, the oxides can be obtained by reduction of the corresponding diarylarsinic acids.

The arylarsine oxides, when allowed to react with an aromatic Grignard reagent, were converted into tetra-arylarsyl oxides, as follows

$$\begin{aligned} 2RAs{=}O + 2\ RMgX &\longrightarrow 2RRAs(OMgX) \\ 2RRAs(OMgX) + 2H_2O &\longrightarrow RRAs{-}O{-}AsRR \\ 2RAs{=}O + 2R'MgX &\longrightarrow 2RR'As(OMgX) \\ 2RR'As(OMgX) + 2H_2O &\longrightarrow RR'As{-}O{-}AsR'R \end{aligned}$$

The simple tetra-arylarsyl oxides were obtained directly from the reaction mixture in crystalline form. The mixed oxides, however, could be isolated only in the form of oils which would not crystallize. These products were treated with chlorine,[5] the crystalline tetrachlorides hydrolyzed to the arsinic acids, the latter reduced and the reduction products

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[1] This paper represents the second part of a dissertation submitted to the Graduate School by Mr. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Parke, Davis and Company Fellow, 1927–1929.

[3] Blicke and Smith, THIS JOURNAL, **51**, 1558 (1929).

[4] Pfeiffer and Truskier, *Ber.*, **37**, 1127 (1904).

[5] In some instances the tetra-arylarsyl oxides were oxidized directly to the diarylarsinic acids by means of warm alkaline hydrogen peroxide.

isolated in the form of the diarylarsyl halides. The latter when hydrolyzed yielded the pure tetra-arylarsyl oxides

$$\mathrm{RR'As{-}O{-}AsRR'} \longrightarrow \mathrm{RR'As(Cl_2){-}O{-}As(Cl_2)R'R} \longrightarrow \mathrm{2RR'As(O)OH}$$
$$\mathrm{2RR'AsCl} \longrightarrow \mathrm{RR'As{-}O{-}AsR'R}$$

Experimental Part

Preparation of Mercury Diaryls

General Procedure.—The Grignard reagent was prepared in a liter, three-necked flask from 0.4 mole of the aryl halide, 0.4 of an atomic equivalent of magnesium and 200 cc. of ether. A mechanical stirrer was introduced and the arylmagnesium halide diluted with 100 cc. of dry benzene. Forty-eight g. (0.18 mole) of dry mercuric chloride was added, cautiously, in four portions during the course of an hour with rapid stirring; the stirring was continued for eight hours. The reaction mixture, which consisted of the mercury diaryl and the arylmercuric halide, was treated with ice and a small amount of hydrochloric acid. In the case of mercury diphenyl, the ether-benzene layer was decanted, filtered and dried with fused sodium sulfate. The solvent was removed and the residue washed with petroleum ether (40–60°). In the preparation of mercury ditolyl only a small amount of the substance is present in the ether-benzene layer and in the case of mercury dianisyl and mercury dinaphthyl practically all of the material is found in the reaction mixture as a precipitate. In the latter instance the dry mixture of the mercury diaryl and the arylmercuric halide was placed in a Soxhlet apparatus and the diaryl mercury extracted with benzene.

TABLE I

MERCURY DIARYLS

	Diphenyl[a]	Di-*p*-tolyl[b]	Di-*p*-anisyl[b]	Di-α-naphthyl[c]
M. p., °C.	121	235–238	198–200	240–243
Yield, %	75	70	62	90

[a] Pfeiffer and Truskier, ref. 4, obtained a 42% yield; m. p. 120°. [b] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, **1921**. [c] Matsumiya, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **8**, 394 (1925), obtained this compound from α-naphthylmagnesium bromide and α-naphthyl mercuric chloride in 69% yield.

Preparation of Arylarsine Oxides

General Procedures (a).—The mercury diaryl was heated with one and one-half times the theoretical amount of freshly distilled arsenic trichloride for three hours at 130–140°. The reaction mixture was extracted with benzene and filtered. After removal of most of the benzene on a steam-bath, the mixture was distilled under diminished pressure in an atmosphere of nitrogen until the excess arsenic trichloride had been removed. The crude aryldichloro-arsine was added to a warm 10% solution of sodium hydroxide with rapid stirring; sufficient alkali should be used to dissolve all of the arylarsine oxide formed. The solution was filtered from mercury compounds through a Jena filter. The alkaline filtrate was neutralized, the precipitate washed by decantation and then filtered.

The oxides, with the exception of the naphthyl compound, were dissolved in hot benzene and an equal volume of absolute ether added to the cold benzene solution. The oxides precipitated slowly. The naphthylarsine oxide was obtained in a pure state in the following manner: the crude oxide was suspended in benzene, treated with dry hydrogen chloride and the solution of naphthyldichloro-arsine heated until the solvent was removed. A small amount of petroleum ether (40–60°) was added to the oily residue. The latter became crystalline and the material was then recrystallized from petroleum ether; m. p. 70–72°.[6] Upon hydrolysis of the dichloride there was obtained pure naphthylarsine oxide.

(b) Sulfur dioxide was passed into a mixture prepared from one part of the arylarsinic acid,[7] five parts of methyl alcohol, two parts of concd. hydrochloric acid and about 0.1 g. of potassium iodide dissolved in a small amount of water. The greater part of the aryldichloro-arsine formed precipitated as an oil. Water was added to precipitate the chloride completely and after decantation of the aqueous layer the oil was washed thoroughly with water. The oily chloride was treated with warm 10% sodium hydroxide until a clear solution was obtained. The latter was neutralized, whereupon the arylarsine oxide precipitated.

TABLE II

ARYLARSINE OXIDES

	Phenyl	*p*-Tolyl	*p*-Anisyl	α-Naphthyl
M. p., °C.	144–146[a]	188–190[b]	114–116[c]	245[d]
Yield (method a),[e] %	60	.....	.....	60
Yield (method b),[f] %	80	87	90	..

[a] Michaelis, *Ber.*, **10**, 623 (1877), recorded the melting point as 119–120°. Gryszkiewicz-Trochimowski, Mateyak and Zablotscki, *Bull. soc. chim.*, [4] **41**, 1327 (1927), state that the substance melts at 129–130° when prepared by hydrolysis of phenyldicyano-arsine. [b] La Coste and Michaelis, *Ann.*, **201**, 257 (1880), found the melting point to be 156°. Tolyldichloro-arsine, from which this oxide was prepared by hydrolysis, was analyzed. Calcd. for $C_7H_7AsCl_2$: Cl, 29.95. Found: 29.87, 29.65. [c] Michaelis and Weitz, *Ber.*, **20**, 51 (1887), described this substance as a crystalline crust but recorded no melting point. When this compound is recrystallized from a mixture of benzene and ether, it melts at 93–95° and seems to lose solvent of crystallization. After it has been heated it melts at 114–116°. The latter melting point was obtained when the compound was recrystallized from a mixture of chloroform and ether. [d] If the oxide is dissolved in alkali, precipitated with an acid and then air dried it melts at 245°. After recrystallization from tetralin the melting point was 206–210°. When the compound obtained from tetralin was heated with benzene the melting point was 185–190°. Solvent of crystallization can be seen to escape from the melting-point tube when the latter is heated. [e] The yield is based on the diaryl mercury compound. [f] The yield is based on the arylarsinic acid which had been recrystallized from water.

Interaction of Arylmagnesium Halides and Arylarsine Oxides

General Procedure.—Three hundredths of a mole of the arylarsine oxide was dissolved in 100 cc. of dry benzene, the solution cooled with ice and stirred rapidly. Forty-five hundredths of a mole of the Grignard reagent was then added. After one-half hour the ice-bath was removed and the mixture was stirred for four hours longer. After twelve hours the reaction mixture was decomposed with ice and a small amount of acetic acid, the ether–benzene layer separated, washed with 10% sodium hydroxide and then dried over fused sodium sulfate. The solvents were removed and the oily residue, which could not be obtained in crystalline form in the case of the mixed tetra-arylarsyl oxides, RR'As—O—AsR'R, was dissolved in absolute ether and the solution saturated with chlorine. The tetrachloro derivative of the tetra-arylarsyl oxide precipitated to some extent in the form of an oil which soon became crystalline. The solvent was removed from the mixture and the residue treated with 5% sodium hydroxide

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[6] Gryszkiewicz-Trochimowski, Mateyak and Zablotscki, *Bull. soc. chim.*, [4] **41**, 1328 (1927), record the melting point as 69.5–70°.

[7] The arylarsinic acids were all prepared according to the method of Schmidt, *Ann.*, **421**, 169 (1920).

solution to convert the tetrachloride into the arsinic acid. The alkaline solution of the latter substance was extracted with ether to remove by-products, the solution heated on a steam-bath to remove dissolved ether and then neutralized, whereupon the arsinic acid precipitated in the form of a gum; after some time the latter became solid. The crude arsinic acid was boiled with acetone, the solution cooled and then filtered. This process was repeated several times. The arsinic acid dissolves in the acetone only to a slight extent but the by-products in the crude acid are much more soluble. Phenylbiphenylarsinic acid can be recrystallized from alcohol.

The diarylarsinic acid was then converted into the diarylarsyl chloride by the action of sulfur dioxide and hydrochloric acid in the same manner as described above under general procedure (b). The diarylarsyl chloride precipitated immediately in some cases as an oil, in other instances as a solid. The chloride was then heated with alcoholic sodium hydroxide, whereby it was converted into the tetra-arylarsyl oxide.

TABLE III

DIARYLARSINIC ACIDS[a]

	M. p., °C.	Formula	Arsenic analyses[c] Calcd.	Found
Phenyl-*p*-tolyl	148-150[b]	$C_{13}H_{13}AsO_2$	27.17	27.65
Phenyl-*p*-anisyl	167-169	$C_{13}H_{13}AsO_3$	25.68	26.08
Phenyl-α-naphthyl	175-176	$C_{16}H_{13}AsO_2$	24.03	24.87
Phenylbiphenyl	218-220	$C_{18}H_{15}AsO_2$	22.20	22.10
p-Anisylbiphenyl	228-231	$C_{19}H_{17}AsO_3$	20.38	20.59

[a] All of the diarylarsinic acids are practically insoluble in hot acetone, soluble in a mixture of alcohol and hydrochloric acid, soluble in hot benzene and only slightly soluble in hot water. [b] Michaelis, *Ann.*, **321**, 157 (1902), recorded the melting point as 158-160°. [c] Ewin, *J. Chem. Soc.*, **109**, 1356 (1916).

TABLE IV

DIARYLARSYL CHLORIDES

	M. p., °C.	Formula	Chlorine analyses (Volhard) Calcd.	Found
Phenyl-*p*-tolyl[a]	Oil	$C_{13}H_{12}AsCl$	12.73	12.67
Phenyl-*p*-anisyl	Oil	$C_{13}H_{12}OAsCl$	12.04	12.26
Phenyl-α-naphthyl	Oil	$C_{16}H_{12}AsCl$	11.27	11.12
Phenylbiphenyl	83-85°	$C_{18}H_{14}AsCl$	10.41	10.31
p-Anisylbiphenyl	Oil	$C_{19}H_{16}OAsCl$	9.57	10.01

[a] Michaelis, Table III, footnote *b*, states that this substance is an oil.

TABLE V

TETRA-ARYLARSYL OXIDES

	Reagents for the preparation Oxide	Mg compound	M. p., °C.
Diphenyl-di-*p*-tolyl[a]	Phenylarsine	Phenyl-Mg-bromide	75-77
Diphenyl-di-*p*-anisyl	Phenylarsine	Anisyl-Mg-iodide	Oil
Diphenyl-di-α-naphthyl	Phenylarsine	Naphthyl-Mg-bromide	Oil
Diphenyldibiphenyl	Phenylarsine	Biphenyl-Mg-bromide	124-126
Di-*p*-anisyldibiphenyl	Anisylarsine	Biphenyl-Mg-bromide	Oil
Tetra-*p*-tolyl	Tolylarsine	Tolyl-Mg-bromide	108
Tetra-*p*-anisyl	Anisylarsine	Anisyl-Mg-iodide	128-129
Tetra-α-naphthyl	Naphthylarsine	Naphthyl-Mg-bromide	250-251

[a] Michaelis, footnote *a*, Table II, prepared the substance by the hydrolysis of the chloride, which had been obtained by heating phenyldichloro-arsine with an excess of ditolyl-mercury. He described it as being an oil.

Summary

1. The preparation of diphenyl, di-*p*-tolyl, di-*p*-anisyl and di-α-naphthyl mercury from the interaction of an arylmagnesium halide and mercuric chloride has been described.

2. Phenyl-, *p*-tolyl-, *p*-anisyl- and α-naphthylarsine oxide have been prepared. Two methods of preparation were used: (a) the diaryl mercury compound was heated with arsenic trichloride and the aryldichloroarsine formed was hydrolyzed; (b) the arylarsonic acid was reduced with sulfur dioxide in the presence of hydrochloric acid and the aryldichloroarsine was hydrolyzed.

3. A number of tetra-arylarsyl oxides of the type RR′As—O—AsR′R were prepared from the interaction of an arylarsine oxide and an arylmagnesium halide. In addition several mixed diarylarsinic acids and mixed diarylarsyl chlorides have been described.

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CLEAVAGE OF AZO DYES BY MEANS OF SULFITES. THE CLEAVAGE OF 4-HYDROXY-AZOBENZENE-5-CARBOXYLIC ACID AND OF 3-METHYL-4-HYDROXY-AZOBENZENE-5-CARBOXYLIC ACID

BY KARL H. ENGEL

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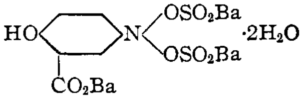
It has been reported in THIS JOURNAL[1] that azo dyes suffer a distinctive cleavage when heated with aqueous sulfite solutions. In a further study of this reaction, the behavior of the above-mentioned dyes has been investigated. The cleavage of these dyes followed closely the reaction course of 4-hydroxy-azobenzene: the primary dye component yielded aniline and an N-sulfonic acid of aniline, the secondary components N-mono- and N-disulfonic acid derivatives of salicylic and of *o*-cresotinic acids, respectively.

4-Hydroxy-azobenzene-5-carboxylic acid yielded an interesting N-disulfonic acid which could be isolated in pure form, as its tribarium salt, represented, presumably, by the formula



$$HO\text{-}C_6H_3(CO_2Ba)\text{-}N(OSO_2Ba)_2\cdot 2H_2O$$

This compound was rather difficultly soluble and perfectly stable in neutral or alkaline solution. It rearranged, in the presence of mineral acids, in a

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[1] Engel, THIS JOURNAL, 51, 2986 (1929).