CLIV.—*The Reactions of Substituted Ammonium Aryloxides and of Related Compounds. Part I. The Preparation and Thermal Decomposition of Some Tetrasubstituted Ammonium Aryloxides.*

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Compounds of the class described in this communication may be written as of the general type $R_4\overset{+}{N}\}\overset{-}{O}Ar$, and are related to the metallic phenoxides in structure, but differ from these in that the phenoxide radical can only be electrovalently attached to the tetrasubstituted ammonium radical, on the assumption that nitrogen is only capable of quadricovalency, whereas many of the metallic phenoxides may exhibit the physical properties of covalent compounds (*viz.*, the solubility of sodium β-naphthoxide and of sodium *p*-chlorophenoxide in anhydrous ether) (Tijmstra and Eggink, *Ber.*, 1906, **39**, 14; Hantzsch and Mai, *Ber.*, 1895, **28**, 978).

In view of the fact that many of the reactions of phenols in alkaline solution are regarded as being caused by the ionisation of the metallic phenoxide, we thought that such typical processes as the Kolbe–Schmitt carboxylation and the Reimer–Tiemann reaction could with advantage be studied in the ammonium series. In the present communication we describe the preparation of some tetrasubstituted ammonium aryloxides, and their behaviour towards heat, since we required a knowledge of their thermal stability before undertaking an examination of their reactions.

A number of tetrasubstituted ammonium picrates are known, but these are clearly unsuitable for this work. The preparation of *phenyltrimethylammonium* o-*nitrophenoxide* was first attempted, so as to gauge the experimental difficulties likely to be encountered when less acidic phenols were used. We realised that, according to commonly accepted theory, *o*- and *p*-nitrophenoxides are salts of the coloured quinonoid forms, and not therefore true phenoxides. This theory, however, is less satisfactory than is sometimes assumed, for it does not entirely accord with the experimental observations of the action of alkyl halides on silver nitrophenoxides, and does not explain the bright red colour of sodium *m*-nitrophenoxide, nor the existence of orange-red forms of 2 : 4 : 6-tribromophenol and similar compounds (Torrey and Hunter, *Ber.*, 1907, **40**, 4333; Hantzsch and Scholtze, *ibid.*, p. 4881).

Although phenyltrimethylammonium *o*-nitrophenoxide is extremely hygroscopic, it was isolated as a scarlet, highly crystalline substance: the corresponding p-*nitrophenoxide*, also very hygroscopic, was yellow. So far the *m*-nitrophenoxide has remained as a deep red oil in spite of all attempts to make it crystallise.

The isolation of *phenyltrimethylammonium phenoxide* proved difficult, but the substance was eventually obtained in quantity. It exhibited true salt-like insolubility in anhydrous ether, but was very soluble in water and in alcohol, and was sufficiently soluble in nitrobenzene to crystallise from this solvent. *Phenyltrimethylammonium α-naphthoxide* was even more difficult to isolate in the pure state, but was finally crystallised from nitrobenzene and also from acetone.

Phenyltrimethylammonium thiophenoxide and *phenyltrimethylarsonium thiophenoxide* have been prepared. Their isolation is much less difficult than that of the above phenoxides.

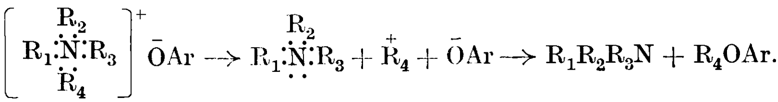
We propose to study all the relevant reactions of the new series of phenoxides in the solid state, in weakly ionising solvents such as nitrobenzene, and in hydroxylic solvents. Preliminary work has already shown that the ammonium phenoxides are very much more reactive than those of the alkali metals. In the present communication, however, we confine our attention to two sets of observations : (1) on the thermal decomposition of the aryloxides and (2) on their interaction with alkyl iodides.

Initial experiments on the thermal decomposition of the phenoxides showed that these compounds undergo particularly smooth and quantitative scission :

$$R_1R_2R_3R_4\overset{+}{N}\}\overset{-}{O}Ar = R_1R_2R_3N + R_4OAr.$$

In fact, in a study of its thermal decomposition a tetrasubstituted ammonium aryloxide may for all practical purposes be regarded as a mixture of its decomposition products, which has to be purified by vacuum distillation. In all the cases examined, thermal decomposition proceeds quantitatively in a few minutes. For example, if phenyltrimethylammonium phenoxide is " distilled " under reduced pressure by means of a heating bath kept at about 120°, dimethylaniline and anisole pass over as rapidly as the apparatus allows, and are obtained in quantitative yield.

A convenient method is thus made available for a study of the mode of decomposition of tetrasubstituted ammonium aryloxides of a number of different types. The course of any such thermal decomposition may be controlled either by the groups R_1, R_2, R_3, and R_4 contained in the ammonium ion, or by the aryl group of the aryloxide ion, but consideration of the probable mechanism of the decomposition suggests that, although the aryloxy-group may affect the *speed* of decomposition, it is unlikely to have any effect on the *sense* of that decomposition. The simplest expression for the decomposition appears to be as below :



$$\left[\begin{array}{c} R_2 \\ R_1\!:\!\ddot{\underset{..}{N}}\!:\!R_3 \\ R_4 \end{array}\right]^{+} \overset{-}{O}Ar \longrightarrow \begin{array}{c} R_2 \\ R_1\!:\!\ddot{\underset{..}{N}}\!:\!R_3 \end{array} + \overset{+}{R_4} + \overset{-}{O}Ar \longrightarrow R_1R_2R_3N + R_4OAr.$$

That is, since the ammonium ion is forced to eject one of its R components, it expels that one which is least firmly attached. This ejected fragment R_4 will have a brief existence as a positive ion, and neutrality will be attained by its combination with the aryloxide ion. It is known that during the thermal decomposition of lead tetramethyl, methyl ions do persist during a short time (Paneth and Hofeditz, *Ber.*, 1929, **62**, 1335). Although it is possible that the aryloxide ion may have preference for one or other of the groups R, it seems clear that the main controlling mechanism is the initial decomposition of the ammonium complex.

The thermal decomposition of phenyltrimethylammonium phenoxide, *o*-, *m*-, and *p*-nitrophenoxide, 2 : 4-*dinitrophenoxide*, α-naphthoxide, and *m*-4-xylyloxide leads in every instance to dimethylaniline and the methyl ether of the phenol. In no case was a detectable quantity of the diphenyl ether type formed. The thermal decomposition of *phenylbenzyldimethylammonium* o-*nitro*- and 2 : 4-*dinitrophenoxide* and the xylyloxide all give dimethylaniline, the benzyl radical in each case undergoing most ready ejection from the ammonium ion, and appearing as the corresponding benzyl aryl ether. To a limited extent, these results suggest that even profound modification of the aryloxide does not have any effect on the course of the decomposition.

Thermal decomposition of *phenyldimethylethylammonium* 2 : 4-*dinitrophenoxide*, on the other hand, is not unidirectional, dimethylaniline, methylethylaniline, 2 : 4-dinitroanisole and 2 : 4-dinitrophenetole all being formed.

Phenyltrimethylammonium thiophenoxide undergoes quantitative thermal decomposition into dimethylaniline and thioanisole. When phenyltrimethylarsonium thiophenoxide is heated, slight sublimation takes place, but again quantitative decomposition occurs, giving phenyldimethylarsine and thioanisole.

We have also examined the effect of boiling aqueous solutions of some tetrasubstituted ammonium aryloxides. It was not surprising to find that phenyltrimethylammonium phenoxide was rapidly and completely converted, when boiled in 10% aqueous solution, into dimethylaniline, phenol and methyl alcohol, and that no anisole could be detected, but it was not anticipated that prolonged boiling, followed by evaporation to dryness of the corresponding *p*-nitrophenoxide, would be unaccompanied by appreciable hydrolysis or decomposition, which was our experimental observation. Experiments are in progress on the effect of limited amounts of water and other solvents on the decomposition of the phenoxides.

After the above work was completed, we found that Hanhart and Ingold (J., 1927, 997), in their study of a different problem, had decomposed trimethyl-*n*-propylammonium phenoxide and *m*-nitrophenoxide, without attempting to isolate them. We have been in communication with Professor Ingold, who expressed his willingness for us to proceed with our work.

Tetrasubstituted ammonium aryloxides react with methyl (ethyl) iodide to give the quaternary ammonium iodide and a phenolic ether :

$$\overset{+}{\mathrm{NR}_4}\}\overset{-}{\mathrm{O}}\mathrm{Ar} + \mathrm{MeI} = \overset{+}{\mathrm{NR}_4}\}\overset{-}{\mathrm{I}} + \mathrm{MeOAr}$$

and here the speed of the reaction is affected largely by the nature of the groups substituted in the aryloxide ion.

Of the phenyltrimethylammonium phenoxides at our disposal, the *m*-4-xylyloxide and the α-naphthoxide reacted vigorously with cold methyl iodide, and the phenoxide almost as readily. The *o*-nitrophenoxide reacted completely with methyl iodide after five minutes' boiling in alcoholic solution, whereas the 2 : 4-dinitrophenoxide was unaffected by this treatment, although, after being boiled in methyl-alcoholic solution with methyl iodide for three hours, it was entirely converted into the quaternary iodide and dinitroanisole. These results indicate quite definitely that substitution in the aryloxide ion nucleus of electron-attracting groups decreases the rate of reaction with methyl iodide, but groups having electron-donating properties increase it.

Phenyltrimethylarsonium thiophenoxide reacts instantaneously with cold methyl iodide to give phenyltrimethylarsonium iodide and thioanisole. Phenyltrimethylammonium thiophenoxide reacts readily with cold methyl iodide to give the analogous products.

We hope shortly to report on the action of halogens, chloroform, and other compounds on the new phenoxides.

EXPERIMENTAL.

Phenyltrimethylammonium o-*Nitrophenoxide.*—A concentrated warm aqueous solution of phenyltrimethylammonium iodide (1 mol.) was treated with freshly precipitated silver oxide until the black oxide was clearly visible on shaking, and the solution gave no test for iodide. The liquid was filtered and, after being treated with 1 mol. of *o*-nitrophenol, was evaporated under reduced pressure in a bath kept at 50—60°, alcohol being added from time to time to accelerate evaporation. When no further diminution in volume occurred, the syrupy red product was dissolved in a little absolute alcohol, and anhydrous ether was added until crystallisation set in, whereupon excess of ether was added, and the precipitate was rapidly collected and washed with ether. After being dried in a vacuum over sulphuric acid, the o-*nitrophenoxide* was obtained as scarlet plates, m. p. 117—117·5° (Found: N, 10·0. $C_{15}H_{18}O_3N_2$ requires N, 10·2%). The nitrophenoxide is excessively hygroscopic, but can be kept for an indefinite period in a dry atmosphere. It may also be prepared by the interaction of phenyltrimethylammonium iodide and silver *o*-nitrophenoxide in boiling alcoholic solution.

The nitrophenoxide was warmed for 5 minutes with a methyl-alcoholic solution of methyl iodide. Ether was then added, and the crystalline precipitate was identified as phenyltrimethylammonium iodide m. p. 225°.

Thermal Decomposition of Phenyltrimethylammonium o-*Nitrophenoxide.*—The phenoxide (7·5 g.) was heated at 180° in a large boiling tube fitted with a calcium chloride tube. After a few minutes, dimethylaniline began to form, and after an hour the decomposition was complete. The product was dissolved in benzene and the solution extracted with 20% hydrochloric acid. From the benzene solution were obtained 3·5 g. of *o*-nitroanisole, and from the acid layer, by treatment with ammonium hydroxide, followed by extraction with benzene, the dimethylaniline was isolated. It was converted into the methiodide, of which 5 g. were obtained, m. p. 229—230°.

Phenyltrimethylammonium p-*Nitrophenoxide.*—The preparation of this compound was carried out similarly to that of the *o*-isomeride. The phenoxide was obtained crystalline by adding anhydrous ether to the concentrated alcoholic solution, and formed yellow prismatic needles, m. p. 118—119°, with considerable previous softening. It is very hygroscopic, but may be crystallised (yellow needles) from nitrobenzene if it has previously been well dried (Found : N, 10·0. Calc. : N, 10·2%). Decomposition at 170° by the process used for the *o*-isomeride gave almost theoretical yields of dimethylaniline and *p*-nitroanisole.

The *p*-nitrophenoxide reacts rapidly with potassium iodide in alcoholic solution to give phenyltrimethylammonium iodide. A solution of 2 g. of the *p*-phenoxide in 40 c.c. of water was boiled under reflux for 4 hours. No odour of dimethylaniline was produced, and the solution was then evaporated to dryness on the water-bath. The residue became solid, after being dried in a vacuum over phosphoric oxide, and then melted at 115—120°. It produced no depression of the m. p. of the original material.

Methyl iodide slowly converts phenyltrimethylammonium *p*-nitrophenoxide in boiling alcoholic solution into the quaternary iodide and *p*-nitroanisole.

Phenyltrimethylammonium m-*Nitrophenoxide.*—This substance was obtained as a deep red oil, which, even after prolonged extraction with anhydrous ether and vacuum desiccation over phosphoric oxide, refused to crystallise. By this process, however, all impurities are effectively removed.

Thermal decomposition of the phenoxide by the process used above gave almost theoretical yields of dimethylaniline and *m*-nitroanisole (m. p. 36° when crude).

Phenyltrimethylammonium 2 : 4-*Dinitrophenoxide.*—This substance crystallised from the concentrated alcoholic solution obtained at the evaporation stage of its preparation by the usual process. It crystallised from absolute alcohol in yellow prisms, softening at 90°

and melting at 121—123° (Found: N, 13·2. $C_{15}H_{17}O_5N_3$ requires N, 13·2%).

The phenoxide was heated for ¼ hour at 135—140°. On cooling, it was found to be unchanged. At temperatures up to 165°, the same result was obtained, even after 1 hour's heating. At 170—175°, decomposition took place in 1 hour, and at 180° or higher temperatures, profound decomposition set in suddenly with charring.

The successful decomposition at 170—175° gave a mixture which was treated with 20% hydrochloric acid. The 2 : 4-dinitroanisole obtained was identified by comparison with an authentic specimen and by conversion into 2 : 4-dinitrophenylpiperidine. The dimethylaniline produced was identified by its b. p. and by conversion into the methiodide.

A methyl-alcoholic solution of the 2 : 4-dinitrophenoxide and methyl iodide was kept at 50—60° for an hour: the phenoxide was recovered unchanged. After 3 hours' boiling, however, theoretical yields were obtained of phenyltrimethylammonium iodide, m. p. 225°, and of 2 : 4-dinitroanisole, which was identified by conversion into 2 : 4-dinitrophenylpiperidine.

Phenyltrimethylammonium Phenoxide.—An aqueous solution of 1 mol. of phenyltrimethylammonium hydroxide was concentrated under reduced pressure at about 50°, with occasional addition of absolute alcohol. An alcoholic solution of phenol (1 mol.) was then added, and the evaporation continued. When no more alcohol came off, the syrup was dissolved in alcohol and excess of anhydrous ether was added. The *phenoxide*, which separated in pearly plates, was dried in a vacuum over sulphuric acid and phosphoric oxide, and then melted at 58—59°. After being crystallised from nitrobenzene, with subsequent washing with light petroleum (b. p. 60—80°), it melted at 75—76° (Found: N, 6·0. $C_{15}H_{19}ON$ requires N, 6·1%). The substance also crystallised from acetone–light petroleum in white plates.

A solution of 2 g. of the phenoxide in 20 c.c. of water was boiled for 2 hours under reflux. The mixture was then freed by routine methods from basic and acidic substances. An ethereal solution obtained, which must have contained any anisole, was evaporated, and left no appreciable residue, although the odour of anisole was detected. The amount of anisole produced was less than 0·1 g. Dimethylaniline, phenol and methyl alcohol were found in the expected extracts.

The phenoxide reacted with cold methyl iodide, and when heated for a few minutes with alcoholic methyl iodide, was quantitatively converted into phenyltrimethylammonium iodide.

The decomposition of the phenoxide was carried out as follows:

17·5 g. were placed in a Claisen distilling flask, which was evacuated, and gradually heated at 120° during 10 minutes. Distillation was then complete, and no appreciable residue was left after the flask had been warmed with a flame. The distillate (17 g.) was dissolved in ether, and extracted with 20% hydrochloric acid. The acid solution was extracted with ether, and the ethereal solution with dilute hydrochloric acid. From the ethereal extracts were obtained, after distillation, 8 g. of pure anisole; and from the acid solutions, after treatment with ammonium hydroxide, extraction and distillation, 8 g. of pure dimethylaniline. The calculated ratio of anisole to base is 107 : 121.

Phenyltrimethylammonium m-4-*Xylyloxide.*—Evaporation of the solution obtained in the usual manner gave a colourless syrup, which was washed with absolute ether and kept in a vacuum over concentrated sulphuric acid and phosphoric oxide. It decomposed, in a bath kept at 110°, without leaving a weighable residue. From 21 g. of syrupy xylyloxide, 20 g. of distillate were obtained, and this yielded 10 g. of pure *m*-xylyl methyl ether, b. p. 180—190°, and 9 g. of pure dimethylaniline. The calculated ratio of ether to base is 136 : 121.

The xylyloxide reacted vigorously with cold methyl iodide to give phenyltrimethylammonium iodide and xylyl methyl ether.

Phenyltrimethylammonium α-Naphthoxide.—This substance, which was obtained in the usual manner, crystallised when its concentrated alcoholic solution was cooled and left in a vacuum over concentrated sulphuric acid and phosphoric oxide. It was recrystallised from nitrobenzene or from acetone, from which it separated in white needles and plates, m. p. 107—108° (Found: N, 4·8. $C_{19}H_{21}ON$ requires N, 5·0%). When the alcoholic solution was allowed to concentrate slowly over concentrated sulphuric acid, large square flat plates were obtained.

The naphthoxide reacted with cold methyl iodide, and on addition of alcohol and warming, the reaction became quantitative. Phenyltrimethylammonium iodide and α-naphthyl methyl ether were identified as the sole products. Decomposition of the naphthoxide (14 g.) occurred at 140—150°, and gave 13 g. of total distillate. This, after the usual separation process, yielded 5 g. of dimethylaniline and 6 g. of α-naphthyl methyl ether, whereas the calculated ratio of base to ether is 121 : 158.

Phenyldimethylethylammonium 2 : 4-*Dinitrophenoxide.*—This substance was prepared as usual, and crystallised from alcohol–ether in small mustard-coloured needles, m. p. 55—57° (Found: N, 12·6. $C_{16}H_{19}O_5N_3$ requires N, 12·6%).

This phenoxide is not particularly hygroscopic. It did not react with methyl iodide in boiling alcoholic solution after 5 minutes. Decomposition of 5 g. of the phenoxide occurred at 170°, and was complete in one hour. From the products were obtained 2·5 g. of acid-insoluble material, m. p. 39—50°, and 2 g. of a mixture of bases, b. p. 190—200°. The acid-insoluble material was heated with twice its weight of piperidine, excess of 20% hydrochloric acid was added, and the precipitated solid was collected (3 g.). It melted at 91—94° and was almost pure 2 : 4-dinitrophenylpiperidine. The filtrate contained both methyl and ethyl alcohol. The mixture of bases was submitted to micro-distillation; the lower-boiling fraction was converted into the chloroplatinate (Found : Pt, 29·6. Calc. for the chloroplatinate of dimethylaniline: Pt, 29·9%). The higher-boiling fraction was converted into the methiodide, which melted at 133—136°, and at 132—134° when mixed with phenyldimethylethylammonium iodide (m. p. 132—133°), but at below 115° when mixed with phenyltrimethylammonium iodide. Dimethyl- and methylethyl-aniline were therefore both formed in the above decomposition, together with dinitroanisole and dinitrophenetole.

Phenylbenzyldimethylammonium o-*Nitrophenoxide*.—This substance crystallised in vermilion needles when dry ether was added to the concentrated alcoholic solution, and had m. p. 91—92° (Found : N, 8·05. $C_{12}H_{22}O_3N_2$ requires N, 8·0%).

Decomposition of 12 g. of the phenoxide occurred at 155—165°, and gave a mixture of products, b. p. 92—220°/28 mm., consisting of 4 g. of dimethylaniline and 7·5 g. of benzyl *o*-nitrophenyl ether. The calculated ratio of base to ether is 121 : 229.

Phenylbenzyldimethylammonium 2 : 4-*dinitrophenoxide* crystallised from alcohol–ether in fern-like aggregates of mustard-coloured needles, m. p. 138—138·5° (Found : N, 10·5. $C_{21}H_{21}O_5N_3$ requires N, 10·6%). It is not hygroscopic.

Phenylbenzyldimethylammonium *m*-4-xylyloxide was not obtained crystalline, but was freed from impurities by extraction with absolute alcohol and anhydrous ether. After being left in a vacuum over concentrated sulphuric acid and phosphoric oxide, it was decomposed. Decomposition was not marked below 145—150°, and was effected at 175—185°. The portion of the product which was soluble in acid was pure dimethylaniline. No benzylmethylaniline was present. The acid-insoluble product was benzyl xylyl ether.

Phenyltrimethylammonium Thiophenoxide.—When the aqueous-alcoholic solution of the quaternary hydroxide and thiophenol was concentrated, the *thiophenoxide* crystallised. It was recrystallised by addition of ether to an alcoholic solution, and formed white plates, m. p. 83—83·5° (Found : N, 5·7. $C_{14}H_{19}NS$ requires N, 5·7%). It is not hygroscopic. Ethyl iodide reacted vigorously with it in the cold, phenyltrimethylammonium iodide, m. p. 227—228°, being formed.

Decomposition of the thiophenoxide (20 g.) took place at 125°. Within 5 minutes, 18 g. of liquid distilled at 80—85°/14 mm. This, after separation, gave 8·5 g. of thioanisole and 8 g. of dimethylaniline, whereas these two should have been formed in the proportion of 124 : 121.

Phenyltrimethylarsonium Thiophenoxide.—We first attempted to prepare this substance by heating silver thiophenoxide with an alcoholic solution of phenyltrimethylarsonium iodide, but after several hours' boiling, the latter was recovered almost unchanged. By evaporation of the quaternary hydroxide with thiophenol, the *thiophenoxide* was readily obtained; it crystallised from alcohol on addition of ether in white leaflets, m. p. 144—145°, and was soluble in water or alcohol, but insoluble in ether (Found: S, 10·5. $C_{15}H_{19}SAs$ requires S, 10·5%).

Although the phenyldimethylarsine required for the preparation of phenyltrimethylarsonium iodide is very readily obtained from dimethyliodoarsine (Burrows and Turner, J., 1920, **117**, 1378), we desired to prepare it from phenyldichloroarsine. Winmill (J., 1912, **101**, 723) treated this substance with magnesium methyl iodide in a mixture of ether and light petroleum (b. p. 30—40°) and obtained a 75% yield. We find that higher-boiling petroleum (b. p. 60—80°) can be used, and that if 4 molecular proportions of Grignard reagent are taken, the yield of pure phenyldimethylarsine is over 90%, even in small preparations. Starting with 22 g. of phenyldichloroarsine, it is thus possible to obtain 27—28 g. of the quaternary arsonium iodide.

The thiophenoxide (15 g.) began to decompose at 160°, and, apart from a little sublimation, was completely converted in 10 minutes into a mixture, b. p. 71—72°/11 mm., of phenyldimethylarsine and thioanisole (14·5 g.). 5 G. of this were dissolved in absolute alcohol, methyl iodide was added, and the mixture was left for 3 hours. Absolute ether was added, and the precipitated phenyltrimethylarsonium iodide was dried at 100° (6 g., corresponding to 2·8 g. of phenyldimethylarsine).

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