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Abstract

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ON THE INTERACTION OF CERTAIN SUBSTITUTED TRIARYLCHLORO- AND BROMOMETHANES WITH SALTS OF DIALKYLPHOSPHOROUS ACIDS

One of us, together with B. A. Arbuzov, in 1929 (^{1}) discovered a new method for obtaining free radicals of the triarylmethyl series by the action of triphenylbromomethane and other triarylbromomethanes in ethereal solution on sodium diethyl phosphite, likewise in ethereal solution, according to the equation:

$$2(C_6H_5)_3CBr + 2NaOP(OC_2H_5)_2 \rightarrow 2NaBr + [(C_2H_5O)_2PO]_2 + 2(C_6H_5)_3C.$$

When triphenylchloromethane is allowed to react with sodium diethyl phosphite under the same conditions, esters of triphenylmethylphosphinic acid are obtained. This reaction was subsequently studied in detail by a number of chemists ($^{2-10}$).

It was shown that, in the case of other triarylhalomethanes, free radicals are obtained only from triarylbromomethanes, and not from triarylchloromethanes (^{4}). Earlier it had been found that, in contrast to other triarylbromomethanes, tri-*p*-anisylbromomethane with sodium diethyl phosphite does not give a free radical. This behavior of tri-*p*-anisylbromomethane prompted us to study in detail the interaction of various substituted triarylchloro- and bromomethanes with salts of dialkylphosphorous acids. In the present communication we set forth the results of our study of the reactions of salts of dialkylphosphorous acids with mono-*p*-anisyldiphenyl-, di-*p*-anisylphenyl-, and tri-*p*-anisylbromomethanes, and with halogen-substituted triarylhalomethanes.

For this purpose we synthesized the following bromides: mono-*p*-anisyldiphenylbromomethane, m.p. 136–138°, di-*p*-anisylphenylbromomethane, m.p. 120–121.5°, and tri-*p*-anisylbromomethane, m.p. 106–108°. When a benzene solution of the bromide, containing a small amount of chloroform for better dissolution, was poured into an ethereal solution of sodium diethyl phosphite, in all cases with methoxy-substituted triarylbromomethanes the diethyl esters of the corresponding phosphinic acids were obtained. The mono-*p*-anisyldiphenylmethylphosphinic ester obtained has m.p. 117.5–118.5°. It was not possible to isolate the di-*p*-anisylphenyl- and tri-*p*-anisylmethylphosphinic esters in pure form. On saponification of them, the corresponding triarylmethylphosphinic acids were obtained, with m.p. 214° and 229–229.5°, respectively.

The phosphinic esters obtained were also synthesized by us through the action of the corresponding bromides on triethyl phosphite. Mono-*p*-anisyldiphenylmethylphosphinic ester has m.p. 117.5–118.5°. Tri-*p*-anisylmethylphosphinic ester has m.p. 139–140.5°. The latter, on saponification, gives the corresponding acid with m.p. 228.5°. From the products of the reaction of triethyl phosphite with di-*p*-anisylphenylbromomethane, followed by saponification, di-*p*-anisylphenylmethylphosphinic acid was obtained, m.p. 213.5–214°.

It is of interest to note that in individual experiments, for example in the case of di-*p*-methoxytriphenylbromomethane, reduction of the bromide to the corresponding di-*p*-methoxytriphenylmethane occurs, m.p. 100° and in yields up to 66%. The conditions necessary for carrying out the reaction with formation of the triarylmethane derivative have not been definitively clarified by us.

Quite unexpectedly, with a certain change in the conditions of the reaction of triarylbromomethanes with sodium diethyl phosphite—namely, when an ethereal solution of sodium diethyl phosphite was poured onto the ground solid crystalline triarylbromomethane—peroxides of the corresponding triarylmethyl radicals were obtained when the reaction was carried out in the presence of air, with the following constants: for mono-*p*-anisyldiphenylmethyl peroxide, m.p. 153–155°; for di-*p*-

anisylphenylmethyl, m.p. 130°, and for tri-*p*-anisylmethyl peroxide, m.p. 125–126°. Under the same conditions, small amounts of esters of triarylmethylphosphinic acids are also observed.

The formation, under the above conditions, of free radicals forming peroxides was confirmed by measurement of the EPR* at the moment of reaction, and by synthesis of the corresponding peroxides by M. Gomberg' s method. It was not possible to isolate tri-*p*-anisylmethyl peroxide when carrying out the reaction according to Gomberg.

Mono-*p*-ethoxyphenyldiphenylbromomethane with sodium diethyl phosphite simultaneously gives mono-*p*-ethoxytriphenylmethyl peroxide, m.p. 125.5°, and the diethyl ester of mono-*p*-ethoxytriphenylmethylphosphinic acid, b.p. 76°/2 mm.

The formation of the free radical when an ethereal solution of sodium diethyl phosphite is added to solid triarylhalomethane takes place, as we have established, also in the case of triphenylchloromethane; moreover, besides triphenylmethyl peroxide, the ester of triphenylmethylphosphinic acid is obtained as the principal product. Di-*p*-anisylphenylchloromethane reacts with sodium diethyl phosphite with formation of a free radical. Peroxides of free radicals are also formed under the action of potassium diethyl phosphite on tri-*p*-anisylbromomethane and mono-*p*-anisyldiphenylbromomethane.

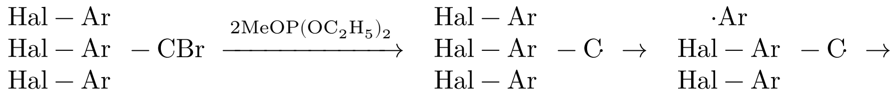
As is seen from the foregoing, the reaction of methoxy-substituted derivatives of triphenylbromo- and triphenylchloromethanes with salts of diethyl phosphorous acid proceeds differently depending both on the nature of the halogen derivative and on the reaction conditions. We also studied the reaction of salts of diethyl phosphorous acid with halogen derivatives of triphenylchloromethane and triphenylbromomethane substituted in the ring, namely tri-*p*-chlorophenylbromomethane, m.p. 143–145°, tri-*p*-bromophenylchloromethane, and *o,p,p*-trichlorophenylmethane.

In all these cases, the formation of free radicals was established by isolation, in small amounts, of peroxides, or by the appearance of signals upon EPR measurement.

Thus, in the case of action on tri-*p*-chlorophenylbromomethane at a ratio of 1 mole to 1 mole, tri-*p*-chlorophenylmethyl peroxide, m.p. 190°, was obtained in an amount up to 8%. This peroxide had previously been obtained by Gomberg (11) in the form of complexes with two molecules of benzene, m.p. 180°. The melting point indicated by Gomberg probably refers to the peroxide after removal of benzene. When the potassium salt of dimethyl phosphorous acid was used, the yield of peroxide increased to 38%. The reaction studied is accompanied by the formation of a large quantity of noncrystallizing products, from which it was not possible to isolate individual compounds.

The complexity of the course of the reaction in the case of ring-substituted halogen derivatives of triphenylchloro- or bromomethanes is evidently explained by the fact that halogens of the benzene ring can apparently also enter into the reaction. Thus, under the action on tri-*p*-bromophenylchloromethane and *o,p,p*-trichlorophenylchloromethane of potassium or sodium diethyl phosphite in a ratio of 1 mole to 4 moles or 1 mole to 3 moles, it was established that, in addition to the chlorine located at the central carbon atom, another 1 to 2½ atoms of halogen of the benzene ring of the triarylhalomethane molecule were cleaved by salts of diethyl phosphorous acid.

Such behavior of halogens located in the benzene ring was previously observed by Gomberg (11–13) and was studied in detail by Bauden (14, 15) in the interaction of halo-substituted chlorides with molecular silver.



$$\begin{array}{l} Hal-Ar \\ Hal-Ar \\ Hal-Ar \end{array} -CBr \xrightarrow{2MeOP(OC_2H_5)_2} \begin{array}{l} Hal-Ar \\ Hal-Ar \\ Hal-Ar \end{array} -C\cdot \rightarrow \begin{array}{l} \cdot Ar \\ Hal-Ar \\ Hal-Ar \end{array} -C\cdot \rightarrow$$

$$\rightarrow (Hal-C_6H_4)_3C-C_6H_4-C(C_6H_4Hal)_2$$

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* The EPR spectra were taken by Yu. V. Yablokov, to whom we express our gratitude.

The proposed scheme, which coincides with Bauld' s scheme for the action of metals on halogen-substituted triphenylchloromethanes, shows the possible direction of the reaction in the presence of an excess of a salt of diethylphosphorous acid. In the initially formed triarylmethyl, as a result of redistribution of electron density, the halogen atom in the ring becomes

Fig. 1

mobile and reacts with a second molecule of the salt of diethylphosphorous acid. The biradical formed reacts with a monoradical, with formation of a new monoradical. As our experiments have shown, with an excess of salts of diethylphosphorous acid, subsequent elimination of other halogen atoms in the benzene ring may also occur.

Fig. 2

The complexity of the course of the reaction in these cases is reflected in the e.p.r. curves. This is evident from the following examples. In the interaction of sodium diethyl phosphite with tri-*p*-chlorophenylbromomethane (in a ratio of 3 mol to 1 mol), at the moment of reaction the curve on the oscilloscope has two peaks: *a* and *b*; then peak *b* gradually disappears (Fig. 1).

In the case of the action of sodium diethyl phosphite on *o,p,p*-trichlorophenylchloromethane (3 mol to 1 mol), the e.p.r. curves have a different character (Fig. 2): at first one peak is formed (1), then a small second peak *b* appears (2). Thereafter peak *b* disappears (3) and a new peak *b* appears again (4, 5), which first grows and then gradually disappears.

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