AMMONIUM PHOSPHONIUM SALTS

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While studying the reactions of tertiary phosphines with Schiff bases in the presence of hydrogen chloride it was shown by us that mixed ammonium phosphonium salts (I) are formed here [1]. The structure

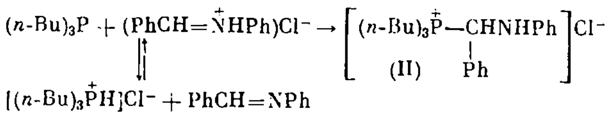
$$R_3P + PhCH{=}NPh \xrightarrow{+HCl} [R_3\overset{+}{P}CH(Ph)\overset{+}{N}H_2Ph]2Cl^- \quad \text{(I)}$$

$$R = n\text{-Bu, Ph}$$

of the obtained compounds was confirmed by the IR and ^{31}P NMR spectral data, while the composition was confirmed by elemental analysis. The IR spectra have absorption bands in the 2600-2700 cm^{-1} region (NH_2 stretching vibrations), while the ^{31}P NMR spectra have signals in the 30-40 ppm region, which is characteristic for phosphonium salts [2]. The ammonium phosphonium salts (I) are apparently formed by attack of the carbon of the azomethine group by the phosphorus atom of the tertiary phosphine to give the intermediate bipolar ions (A), which in solution exist in equilibrium with the starting reactants. When treated with HCl the adducts (A) are stabilized and change to the stable salts (I). It was shown by Hoffmann [3] that

$$R_3P + PhCH{=}N{-}Ph \rightleftarrows [P_3\overset{+}{P}{-}CH(Ph)\bar{N}Ph] \xrightarrow{2HCl} \text{(I)} \quad \text{(A)}$$

the hydrobromides of Schiff bases react with tertiary phosphines to give aminobenzylphosphonium salts. Based on the ^{31}P NMR spectral data, it was established that the reaction of tributylphosphine with benzalaniline hydrochloride gives, besides tributyl(1-anilino)-benzylphosphonium chloride (II) (δP 38 ppm), also the complex of tributylphosphine with HCl, which contains a P—H bond (δP 12 ppm J_{PH} = 480 Hz). The appearance of this complex is evidently related to the intermolecular transfer of a proton from the nitrogen atom of the benzalaniline hydrochloride to the phosphorus atom of tributylphosphine. Consequently, in order



$$(n\text{-Bu})_3P + (PhCH{=}\overset{+}{N}HPh)Cl^- \rightarrow \left[(n\text{-Bu})_3\overset{+}{P}{-}\underset{\displaystyle Ph}{CH}NHPh\right]Cl^- \ \text{(II)}; \quad (n\text{-Bu})_3P + (PhCH{=}\overset{+}{N}HPh)Cl^- \rightleftarrows [(n\text{-Bu})_3\overset{+}{P}H]Cl^- + PhCH{=}NPh$$

to exclude the side reactions of HCl during the synthesis of ammonium phosphonium salts (I) it is necessary to run the reaction in solvents, with slow passage of the HCl and vigorous stirring.

Depending on the structure of the phosphine, the alkylation of aminoalkylphosphines with MeI yields either phosphonium salts [3], ammonium salts [4], or rupture of the P—C bond [5] and subsequent alkylation of the P-containing compound. Cleavage of the P—C bond is also observed when aminomethylphosphines are reacted with acylating agents [6]. Together with this, as was found by us previously [1], it was confirmed in the present paper and recently shown in [6] that bisquaternary ammonium phosphonium salts can also be formed when aminomethylphosphines are reacted with electrophilic reagents.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer either as a film or as a Nujol mull, while the ^{31}P NMR spectra were recorded on a nonserial KGU-4 NMR instrument at a frequency of 10.2 MHz relative to 85% H_3PO_4.

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1-(Tributylphosphonio)benzylphenylammonium Dichloride. To 2.8 g of tributylphosphine was added a solution of 2.3 g of benzalaniline in 10 ml of abs. ether, and then a stream of dry HCl was passed into the vigorously stirred mixture. The oily deposit was separated and washed well with abs. ether. After removing traces of the solvent in vacuo we obtained 5.5 g (87%) of 1-(tributylphosphonio)benzylphenylammonium dichloride, n_D^{20} 1.5263. ^{31}P NMR spectrum: δP + 40 ppm. Found: P 7.03; N 2.95; Cl 15.32%. $C_{25}H_{40}NCl_3P$. Calculated: P 6.79; N 3.07; Cl 15.54%.

1-(Triphenylphosphonio)benzylphenylammonium Dichloride. To a solution of 1.5 g of triphenylphosphine in 20 ml of abs. ether was added a solution of 1 g of benzalaniline in 10 ml of abs. ether, and then a stream of dry HCl was passed into the vigorously stirred mixture. The obtained deposit was separated, washed with abs. ether, dissolved in abs. MeOH, activated carbon was added, the mixture was shaken, filtered, and the filtrate was evaporated under reduced pressure. We obtained 2.55 g (89%) of 1-(triphenylphosphonio)benzylphenylammonium dichloride, mp 56°C. Infrared spectrum (ν, cm^{-1}): 2600-2700 ($\overset{+}{N}H_2$), 3300-3400 (NH), 1438 (PPh). Absorption bands are also present that are characteristic for phenyl rings. ^{31}P NMR spectrum: δP + 38 ppm. Found: P 5.52; N 2.63; Cl 14.12%. $C_{30}H_{28}NPCl_2$. Calculated: P 6.00; N 2.71; Cl 13.73%.

CONCLUSIONS

Ammonium phosphonium salts are formed when tertiary phosphines are reacted with benzalaniline in the presence of dry HCl.

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