SYNTHESIS OF METHYLDIPHENYL- β -KETO- γ -DIPHENYLPHOSPHINYLPROPYLPHOSPHONIUM SALTS

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Compounds containing a phosphinyl group as the X substituent proved to be especially interesting when studying the effect of substituents on the acidity and tautomerism of β -ketophosphonium salts of

general type $[R_3P^+ - CH_2COCH_2X]A^-$. The corresponding phosphonium chloride was obtained by us by the scheme:



The dimethyl ketal of sym-dichloroacetone was reacted with potassium diphenylphosphide in THF; the formed diphenyl- β , β -dimethoxy- γ -chloropropylphosphine (I) was not isolated in the pure state, and instead was oxidized directly with perhydrol to the corresponding phosphine oxide (II). Its structure was confirmed by the data of the NMR and IR spectra. In the NMR spectrum (in CHCl₃) the protons of the CH₃O and CH₂Cl groups appear as singlet signals, with chemical shifts of 3.07 and 3.95 ppm, respectively. Further upfield (δ 2.97 ppm) is observed the doublet signal of the protons of the CH₂ group, attached to phosphorus (J_{CH₂-p 14.5 Hz). The protons of the phenyl rings appear as a complex multiplet (δ 7.3-8.0 ppm). A band at 1185 cm⁻¹, belonging to the P=O group, is present in the IR spectrum (KBr pellet).}

Chloroketal (II) could not be made to react with methyldiphenylphosphine, since the chlorine atom proved to be comparatively inert. Compound (II) was converted by hydrolysis to chloroketone (III). In its NMR spectrum (in CHCl₃), besides the multiplet of the phenyl protons, are observed the singlet signal of the protons of the CH₂Cl group (δ 4.48 ppm) and the doublet of the CH₂ group attached to phosphorus (δ 3.81 ppm and J_{CH₂-P 14.5 Hz). In the IR spectrum of chloroketone (III) are present intense bands at 1725 and 1190 cm⁻¹ of the C= O and P=O groups, respectively.}

Chloroketone (III) is more active than the ketal; it reacted with methyldiphenylphosphine when refluxed in acetonitrile solution, with the formation of methyldiphenyl- β -keto- γ -diphenylphosphinylpropylphosphonium chloride (IVa). Fluoborate (IVb), perchlorate (IVc) and the tetraphenylborate (IVd) were obtained by exchange reactions.

The treatment of chloride (IVa), fluoborate (IVb) or the perchlorate (IVc) with aqueous Na₂CO₃ solution gave the corresponding phosphorane (V). In its IR spectrum is present an intense band at 1545 cm⁻¹, which is characteristic for acylphosphinomethylenes [1, 2], and the band of the P = O group at 1195 cm⁻¹. In the NME spectrum is present the doublet of the methyl protons (δ 2.01 ppm, J_{CH_3-P} 13.5 Hz). The methylene protons appear as a doublet of doublets with δ 3.34 ppm; they couple with the adjacent phosphorus atom, with the constant $J_{CH_2-P(O)}$ 14.5 Hz, and with the nucleus of the other phosphorus atom, with J_{CH_3-P} + 2.3 Hz; the signal of the protons of the methine group is not observed; apparently it falls in the

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region of the signals of the phenyl protons [3]. The validity of assigning the NMR signals was corroborated by the method of double heteronuclear resonance ${}^{31}P{}^{-1}H$.

From phosphorane (V) by the addition of trifluoroacetic and acetic acids were obtained the corresponding phosphonium salts (IVe) and (IVf). In contrast to the other phosphonium salts, phosphonium acetate (IVf) is unstable. The proof of the structure of the phosphonium salts (IVa-e), as well as a study of their behavior in solutions, is given in [4].

EXPERIMENTAL METHOD

Diphenyl- β , β -dimethoxy- γ -chloropropylphosphine Oxide (II). To the potassium diphenylphosphide [5], obtained from 0.06 g-atom of K and 0.03 M of diphenylchlorophosphine in 120 ml of THF, was added 0.03 M of the dimethyl ketal of sym-dichloroacetone in 30 ml of THF. The mixture was heated at 40-45° for 6 h, the THF was removed, the residue was dissolved in 80 ml of benzene, and the solution was washed twice with water. After removal of the benzene, the crude diphenyl- β , β -dimethyl- γ -chloropropylphosphine (I) (0.027 M) in 25 ml of acetone was treated with 0.027 M of H₂O₂ in 4 ml of water. The solution was heated at 50°C for 1 h. Recrystallization from acetone gave 3.5 g (47%) of (II) with mp 176-178°. Found: C 60.20; H 5.80; Cl 10.35; P 9.08%. C₁₇H₂₀ClO₃P. Calculated: C 60.27; H 5.95; Cl 10.47; P 9.14%.

Diphenyl- β -keto- γ -chloropropylphosphine Oxide (III). To a solution of 0.01 M of (II) in 250 ml of acetone at room temperature was added 50 ml of 10 N HCl solution in drops, and the mixture was stirred for 2 h. The acetone was removed and the residue was dissolved in 100 ml of ethyl acetate, and the solution was washed twice with NaHCO₃ solution and 3 times with water. After drying and removal of the solvent we obtained 2.3 g (77%) of (III) with mp 111-113° (ethyl acetate). Found: C 61.44; H 4.82; P 10.27%. C₁₅H₁₄· ·ClO₂P. Calculated: C 61.58; H 4.82; P 10.58%.

<u>Methyldiphenyl- β -keto- γ -diphenylphosphinylpropylphosphonium Chloride (IVa).</u> A solution of 0.004 M of (III) and 0.004 M of methyldiphenylphosphine in 35 ml of acetonitrile was refluxed for 7 h. After removal of the solvent in vacuo the residue was recrystallized from a mixture of alcohol and ether. We obtained 1.42 g (72%) of (IVa) with mp 123-126°. The compound is hygroscopic and forms a crystallohydrate with 1 M of water, which is removed on long drying in vacuo at 100°. Found: Cl 6.89; P 12.28%. C₂₆H₂₇* •ClO₂P. Calculated: Cl 7.19; P 12.57% (dried sample).

Methyldiphenyl-β-keto-γ-diphenylphosphinylpropylphosphonium Fluoborate (IVb). By exchange reaction 0.0017 M of (IVa) and 0.002 M of ammonium fluoborate in aqueous alcohol medium was obtained 0.37 g (40%) of (IVb) with mp 180-182.5° (alcohol-petroleum ether). Found: C 61.86; H 5.03; F 14.11; P 11.28% $C_{28}H_{27}BF_4O_2P_2$. Calculated: C 61.78; H 5.00; F 13.96; P 11.38%.

<u>Methyldiphenyl- β -keto- γ -diphenylphosphinylpropylphosphonium Perchlorate (IVc).</u> In a similar manner, from 0.003 M of (IVa) and 0.003 M of sodium perchlorate in aqueous alcohol medium was obtained 1.17 g (73%) of (IVc) with mp 191-193° (alcohol-petroleum ether). Found: P 11.02%. C₂₈H₂₇ClO₆P₂. Calculated: P 11.13%.

<u>Methyldiphenyl- β -keto- γ -diphenylphosphinylpropylphosphonium Tetraphenylborate (IVd)</u>. In a similar manner, from 0.004 M of (IVa) and 0.04 M of sodium tetraphenylborate in alcohol was obtained 2.66 g (86%) of (IVd) with mp 165-166° (decompn.). Found: C 80.31; H 6.20; B 1.41; P 8.09%. C₅₂H₄₇BO₂P₂. Calculated: C 80.41; H 6.10; B 1.39; P 7.98%.

Methyldiphenyl-β-keto-γ-diphenylphosphinylpropylidenephosphorane (V). To a suspension of 0.004 M of (IVa) in 30 ml of water was added, with stirring, 20 ml of aqueous Na₂CO₃ solution (0.004 M). An oil was obtained. The mixture was stirred at room temperature for 1 h, extracted with ethyl acetate, dried over anhydrous MgSO₄, and a part of the ethyl acetate was distilled off. We isolated 1.32 g (94%) of (V) with mp 160-162°. Found: C 73.56; H 5.80; P 13.52%. C₂₈H₂₆O₂P₂. Calculated: C 73.65; H 5.74; P 13.57%.

Methyldiphenyl-β-keto-γ-diphenylphosphinylpropylphosphonium Trifluoroacetate (IVe). To a solution of 0.001 M of phosphorane (V) in 25 ml of absolute benzene was added a 3-fold excess of CF₃COOH in 5 ml of benzene. The solution was kept at room temperature for 2h, the solvent and excess CF₃COOH were removed, and the residue was dissolved in 20 ml of ethyl acetate. The crystalline phosphonium trifluoroacetate (IVe) was isolated by the gradual addition of 85 ml of petroleum ether. The yield of (IVe) was 0.38 g (67%), mp 169-170°. Found: C 63.12; H 4.85; F 10.38; P 11.04%. C₃₀H₂₇F₃O₄P₂. Calculated: C 63.16; H 4.77; F 9.99; P 10.86%.

 $\frac{\text{Methyldiphenyl-}\beta-\text{keto-}\gamma-\text{diphenylphosphinylpropylphosphonium Acetate (IVf).}_{0.001'' \text{ M of (V) and glacial acetic acid was obtained 0.76 g (84%) of (IVf) with mp 102-104°.}_{C 70.00; H 5.83; P 11.80\%. C_{30}H_{30}O_4P_2. Calculated: C 69.78; H 5.85; P 12.00\%.}$

CONCLUSIONS

1. The synthesis of methyldiphenyl- β -keto- γ -diphenylphosphinylpropylphosphonium chloride was accomplished. The fluoborate, perchlorate and tetraphenylborate were obtained from it by exchange reactions.

2. Methyldiphenyl- β -keto- γ -diphenylphosphinylpropylidenephosphorane was synthesized. The addition of acetic and trifluoroacetic acids to it gave respectively the phosphonium acetate and trifluoro-acetate.

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