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Phosphonioethylation using vinylphosphonium salts have found common use in organic chemistry [1]. On the other hand, propenyltriphenylphosphonium salts, which are much more available, have not been studied sufficiently [2-5]. Propenyltriphenylphosphonium chloride [2] and bromide [2, 3] are formed upon treating the corresponding allylphosphonium salts with Et_3N or (Me₃N⁺CH₂Ph)OH⁻. Allyltriphenylarsonium iodide was shown in our previous work to isomerize to propenyltriphenylarsonium iodide upon the action of Et_3N or Et_2NH [6].

In the present work, we studied the reaction of salt (I) with various amines. The reaction of salt (I) with excess Et_3N in acetonitrile at 20°C gives isomerization to propenyltriphenylphosphonium iodide. The formation of (II) was indicated by the displacement of the chemical shift in the ³¹P NMR spectrum from δ 20.7 ppm for (I) [7] to 18.1 ppm for (II) and the appearance of a methyl proton signal in the PMR spectra at δ 2.35 ppm and IR band for the C=C bond at 1620-1640 cm⁻¹, which is lacking in the spectra of salt (I).

This rearrangement apparently proceeds through an ylid intermediate which adds a proton to convert to salt (II).

$$Ph_{3}P^{+}-CH_{2}-CH \cong CH_{2}I^{-} \xrightarrow{R_{4}N} [Ph_{3}P^{+}-CH - CH - CH_{2}] \xrightarrow{I^{+}+HI} Ph_{3}P^{+}-CH = CH - CH_{3}I^{-}$$
(I)
(I1)

Ammonia and primary and secondary amines react with (I) to give (2-aminopropyl)triphenylphosphonium iodide (III). There is apparently initial isomerization of (I) to (II) and, then, the amines add to (II).



Salts (III) are colorless crystalline compounds. Their structures were demonstrated by elemental analysis and PMR and ³¹P NMR spectral data, which are given in Table 1.

 $R^1 = H$, $R^2 = i - Pr$ (g); $R^1 = H$, $R^2 = cyclo - C_0 H_{11}$ (h).

The PMR spectra show signals corresponding to all the proton types in salts (III). A diastereotopic effect is found for the CH_2 group protons as well as for the allkyl group protons in salts (IIIc)-(IIIh).

EXPERIMENTAL:

All the operations were carried out in absolute solvents. The IR spectra were taken on a UR-20 spectrometer in CH_2Cl_2 . The PMR and ${}^{31}P{}^{1}H{}$ NMR spectra were taken on a Bruker WP-200 spectrometer in CDCl₃. The chemical shifts in the PMR spectra were determined relative to TMS as an internal standard, while the shifts in the ${}^{31}P$ NMR spectra were found relative to H_3PO_4 .

<u>Isomerization of (I) by the Action of Et_3N .</u> A sample of 2 ml Et_3N was added to a solution of 0.5 mmole salt (I) in 3 ml acetonitrile. After 24 h, the mixture was evaporated in vacuum and the residue was washed with ether. The crystalline product was reprecipitated from CH_2Cl_2 by the addition of ether to give salt (II) in 85% yield, mp 201-202°C (aceto-

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	in
	(IIIa)-(IIIh)
،	4
I	Ph _a P+C ¹ ₁₂ C ¹ (C ³ ₃)N
	for
	Data
	Spectral
	NMR
	^{3 1} P
	and
	PMR*

	- ³¹ P NMR, §, ppm		24,1	24,2	24,4	24,6	24,3	24,5	24,6	24,1	
$Ph_3P+CH_3CH(CH_3)N \left\langle I^- (IIIa)-(IIIh) in CDC1_3 R_2 \right\rangle$	PMR spectrum, å, ppm (J, Hz)	s HN	1,55 (2H)	1	I	1	I	1,47 s(1H) 1,38 s(2H)	1,43 s (1H)	1,47 s(1H)	
		н ^{с—} Н7	1	1	0,66 t (6H) (³ / 6,9)	1,2m (4H) 0,74m (2H)	2,63 m (2H) † 3,32 m (2H) †	2,39 d.d.d (1H) † (11,6, 4,8, 6,4) 2,51 d.d.d (1H) †	$ \begin{array}{c} (11, 5, 4, 8, 5, 4) \\ 0.441 & (3H) + (^{3}J 6, 1) \\ 0,80 & d (3H) + (^{3}J 6, 1) \\ \end{array} $	1 (4H), 1,24m (1H), (2H), 2,21m (1H)	
		(HH ⁺ ⁵ , ¹ H ⁺ ⁺	1	1,86 s (6H)	2,27 d. q (2H), (13,4, 6,9) 2,50 d.q (2H), (13,4,	6,9) 2,08 m (2H) 2,46 m (2H)	2,15 m (2H) 2,91 m (2H)	1,97 d.d.d. (1H) (11,6, 4,8,6,3) 2,68 d.d.d (1H) (11,6,	4.8, 6,3) 2,70 sept (1H) (³ 1 6,2)	0.41 m (111), 0.89 m 1,48 m (211), 1,57 m	-8.2 nom (15H).
		H ³ d . d (3H) (³ J _{HH} , ⁴ J _{PH})	1,45 (6,2, 2,6)	1,19 (6,5, 2,9)	1,21 (6,6, 2,2)	1,22 (6,6, 3,0)	1,26 (6,7, 2,9)	1,47 (6,1, 2,9)	1,43 (6,1, 2,9)	1,42 (6,0, 2,9)	ets at 6 7.5-
)ata for		[H ² m (1H)	3,31	3,06	3,17	2,86	2,91	2,95	3,19	3,23	multipl
PMR* and ³¹ P NMR Spectral D		H ¹ † d.d.d (2J _{IIH} , ^{3J} HH, ² JPH)	3,47 (15,5, 4,0, 11,5), 2,00, 45 5, 4,0, 14,5),	$\begin{array}{c} \begin{array}{c} \begin{array}{c} 1,0,0\\ 3,75\\ 3,75\\ 3,87\\ 15,4,10,4,11,9\\ \end{array} \\ 3,87\\ \end{array}$	3,66 (15,2, 4,0, 12,4), 3,78 (15,2, 10,5, 12,4)	3,53 (15,9,3,6, 12,3), 4,08 (15,9, 11,1, 11,7)	3,48 (16,0, 3,5, 12,5), 4,35 (16,0, 10,5, 11,4)	3,38 (15,3, 3,6, 11,0), 4,18 (15,3, 11,1, 11,0)	3,60 (15,5, 4,0, 11,5), 4,05 (15,5, 11,1, 11,7)	3,59 (15,5, 3,8, 11,3), 4,03 (15,5, 11,1 11,4)	otons appear as
	Rt	-N R ^z	NH_2	cH _s	cH _a cH _a cH _a N			$\begin{array}{ccc} {}^{4} & {}^{5} & {}^{6} & {}^{-} & {}^$	cH, −NCH H CH,		- snyl group pro
TABLE 1	7	pound	(IIIa)	(4111)	(IIIc)	(pIII)	(111e)	(111f)	(111g)	(111)	*The phe

The enhanced multiplicity of the signal is due to a diastereotopic effect.

nitrile-ether). Found: C 58.48; H 4.65; P 7.09%. Calculated for $C_{21}H_{20}IP$: C 58.59; H 4.68; P 7.18%. IR spectrum (ν , cm⁻¹): 1610, 1630 (C=C). PMR spectrum (E-Ph₃P⁺CH¹-CH²CH₃³I⁻) (II) (δ , ppm, J, Hz): 2.35 d.d.d (3H³, ²J_{H2H3} = 6.6, ³J_{H1H3} = 1.7, ⁴J_{H3P} = 0.7), 6.69 d.d.q (1H², ³J_{H1H2} = 16.6, ³J_{H2H3} = 6.6, ³J_{H2P} = 21.7), 7.37 d.d.q (1H¹, ³J_{H1H2} = 16.6, ⁴J_{H1H3} = 1.7, ²J_{H1P} = 23.5). ³¹P NMR spectrum (δ , ppm): 18.1.

<u>(2-Aminopropyl)triphenylphosphonium Iodide (IIIa)</u>. A stream of dry NH_3 was bubbled through an ampul containing a solution of 0.7 mmole salt (I) in 15 ml acetonitrile at -65°C until the solution volume is increased by 5 ml. The reaction mixture was maintained in the sealed ampul for 72 h at 20°C. The solvent was removed in vacuum and the residue was reprecipitated twice from acetonitrile by the addition of ether to give (IIIa) in 82 % yield, mp 146-147°C. Found: C 56.47; H 5.34; N 2.96; P 6.96%. Calculated for $C_{21}H_{23}INP$: C 56.38; H 5.40; N 3.13; P 6.92%.

<u>(2-Dimethylaminopropyl)triphenylphosphonium Iodide (IIIb)</u>. A stream of dry Me₂NH was passed into a flask containing a solution of 1.2 mmoles salt (I) in 50 ml acetonitrile at -20°C until the volume of the reaction mixture was increased by 10 ml. The hermetically sealed flask with the reaction mixture was maintained at 20°C for five days and the solvent was removed in vacuum. The precipitate was reprecipitated twice from acetonitrile by the addition of ether. The yield of (IIIb) was 80%, mp 183-185°C. Found: C 58.19; H 6.06; N 2.98; P 6.50%. Calculated for $C_{2.3}H_{2.7}INP$: C 58.12; H 5.75; N 2.97; P 6.51%.

Synthesis of Salts (IIIc)-(IIIh). A mixture of 1.4 mmoles salt (I) in 5 ml acetonitrile and 2 ml amine was heated at 60°C for 7 h and evaporated in vacuum. The residue was washed with ether and dissolved in 3-5 ml CH_2Cl_2 . Salt (III) was precipitated by the addition of ether. Salts (III) were reprecipitated from acetonitrile by the addition of ether.

<u>(2-Diethylaminopropyl)triphenylphosphonium Iodide (IIIc)</u> was obtained in 54% yield, mp 167-168°C. Found: C 59.76; H 6.15; P 5.90%. Calculated for $C_{25}H_{31}INP$: C 59.65; H 6.20; P 6.11%.

 $\frac{(2-\text{Piperidinopropyl})\text{triphenylphosphonium Iodide (IIId)}}{176-177^{\circ}\text{C.}} \text{ Found: C 60.22; H 5.91; N 2.52; P 6.01%. Calculated for C₂₆H₃₁INP: C 60.48; H 6.25; N 2.71; P 6.00%.}$

<u>(2-Morpholinopropyl)triphenylphosphonium Iodide (IIIe)</u> was obtained in 97% yield, mp 216°C. Found: C 58.15; H 5.45; N 3.40; P6.06%. Calculated for $C_{25}H_{29}INOP$: C 58.13; H 5.45; N 2.71; P 5.98%.

 $\frac{[2-(2-\text{Aminoethylamino})\text{propyl}]\text{triphenylphosphonium Iodide (IIIf)}}{\text{yield, mp 170-171°C. Found: C 56.44; H 5.70; N 5.81; P 6.30%. Calculated for C₂₃H₂₇IN₂P: C 56.36; H 5.76; N 5.72; P 6.32%.}$

 $\frac{(2-\text{Isopropylaminopropyl)triphenylphosphonium Iodide (IIIg)}{\text{mp 173-174°C. Found: C 58.84; H 5.90; N 2.73; P 6.36%. Calculated for C₂₄H₂₉INP: C 58.90; H 5.97; N 2.85; P 6.33%.}$

 $\frac{(2-Cyclohexylaminopropyl)triphenylphosphonium Iodide (IIIh)}{mp 167-168°C.}$ was obtained in 90% yield, mp 167-168°C. Found: C 60.76; H 6.10; H 2.67; P 5.90%. Calculated for C₂₇H₃₃INP: C 61.15; H 6.25; N 2.64; P 6.05%.

CONCLUSIONS

1. Allyltriphenylphosphonium iodide rearranges to propenyltriphenylphosphonium iodide in the presence of tertiary amine.

2. Ammonia and primary and secondary amines smoothly add to propenyltriphenylphosphonium iodide to form N-substituted (2-aminopropyl)triphenylphosphonium salts.

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OXIDATION OF ETHYLBENZENE BY ATMOSPHERIC OXYGEN AND IODOSOBENZENE CATALYZED BY CrO3

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Iron or manganese porphyrin complexes [2-4] are usually employed as models of enzyme systems [1], which oxidize saturated and alkylaromatic hydrocarbons [2, 3]. Molecular oxygen is used as the oxidizing agent [5, 6]. Iodosobenzene, C_6H_5IO , may serve as a donor of an oxygen atom transferred by a metal complex catalyst to the substrate [7, 8]. Transition metal complexes with chelating nitrogen-containing ligands have been used as oxygen transfer catalysts [9-11]. The first step in the catalyzed oxidation is presumably the transfer of an oxygen atom [12] to the metal ion with formation of an oxo derivative of the metal in a high oxidation state. Cr(VI) oxo compounds may serve as models for such species. We note that the oxygen atom transfer to chromium porphyrin complexes [13, 14] and to Cr(III) complexes with chelating ligands [11].

In the present work, we report the first results of an investigation of the catalytic properties of CrO_3 . Ethylbenzene was used as the substrate and the reactions were carried out in acetonitrile. In the presence of CrO_3 , ethylbenzene is slowly oxidized to acetophenone by atmospheric oxygen (Fig. 1, curve 1). After about 50 h, 1 mole $C_6H_5COCH_3$ is formed per mole CrO_3 . In the case of higher initial concentrations of ethylbenzene and CrO_3 , the reaction proceeds more rapidly and about 2 moles acetophenone are accumulated per mole CrO_3 after 50 h

(Fig. 1, curve 5). The addition of a solution of α -picolinic acid somewhat accelerates the oxidation (Fig. 1, curve 2), but the reaction proceeds more slowly in the presence of trifluoro-acetic acid (Fig. 1, curve 3). Irradiation above 310 nm markedly accelerates the reaction (Fig. 1, curve 4). Carrying out the reaction in acetonitrile, which was previously distilled in an argon atmosphere and containing traces of oxygen, leads to a decrease in the rate of the thermal reaction by a factor of about 1.5. We note that the electronic spectrum of the solution in the visible region hardly changes over 180 h (the intensity of the absorption at 380 nm drops by only 17%). This invariance apparently indicates that chromium in the oxo derivative catalyzing the reaction does not alter its valence state.

Ethylbenzene in the presence of CrO_3 is much more rapidly oxidized by iodosobenzene. In this case, 0.2 mole acetophenone per mole iodosobenzene is formed over about 80 h, after which there is no further accumulation of the oxidation product (Fig. 2a, curve 1). The addition of α -picolinic acid, which is capable of stabilizing Cr(V) and Cr(IV) oxo compounds [15], charcteristically leads to a sharp increase in the rate of accumulation and yield of acetophenone (Fig. 2a, curve 2). The species formed from CrO_3 and α -picolinic acid does not lose its catalytic activity over a long period and is capable of catalyzing the oxidation of ethylbenzene upon the addition of a new portion of iodosobenzene (Fig. 2b). The orange color of the solution disappears only several hours after mixing of the reagents and the maximum at 380 nm is no longer observed. A Cr(III) derivative may be formed (see the work of Kochi et al. [11]). When the reaction is carried out in acetonitrile subjected to prior distillation in an argon atmosphere, the acetophenone yield after 180 h is reduced by 40%, indicating that oxygen takes part in the oxidation.

Thus, CrO_3 in the presence of α -picolinic acid is a catalyst for the oxidation of ethylbenzene by iodosobenzene in acetonitrile. Further investigation is required to elucidate the mechanism for this reaction.

EXPERIMENTAL

All the reactions were carried out in closed glass vessels with periodic agitation by a magnetic stirrer. The experimental conditions are given in the Fig. 1 legends. After

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