Styrene Forming Elimination Reaction from β-Phenylethylphosphonium Salts+

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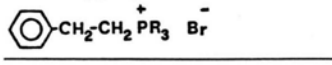
β-Phenylethylphosphonium salts in RO^-/ROH give styrene in amount depending on the steric requirements of the nucleophile and of the salt. The % of styrene formed increases from 22.9 with leaving group PPh_3 to 85.0 with leaving group P(*t*-Bu)$_3$ in *t*-BuOK/*t*-BuOH. Second order rate constants at 30 °C in *t*-BuOK/*t*-BuOH are $1.1 \cdot 10^{-2}$ lm^{-1}s^{-1} with leaving group P(*n*-Bu)$_3$ and $0.96 \cdot 10^{-2}$ lm^{-1}s^{-1} with leaving group P (cyclohexyl)$_3$. The data are consistent with a mechanism of β-elimination.

Phosphonium salts are decomposed in alkaline solution to give tertiary phosphine oxides and hydrocarbons [1–2]. This behaviour is different from that of related ammonium or sulphonium salts which can decompose to form olefins by an elimination reaction [3]. The reason for this difference is that nucleophiles attack the phosphorus atom of a phosphonium salt forming a pentacovalent intermediate which then decomposes to products [4].

It is known [3] that hydrogen activation by a β-phenyl group induces a large rate increase in base promoted elimination reactions from ammonium or sulphonium salts. In order to test if this β-phenyl activation makes competitive the attack of a nucleophile to a β-hydrogen to give olefin with the attack to phosphorus to give hydrocarbons or others products we determined the amount of styrene formed in the basic decomposition of some β-phenylethylphosphonium salts in various base-solvent solutions. The results obtained are reported in the Table. The data of the Table are consistent with competition between nucleophilic attack to phosphorus or to β-hydrogen. Important factors in controlling this competition are steric requirements of the nucleophile and of the salt. In fact it can be seen that from the salt with leaving group PPh_3 a limited amount of styrene is formed and only with the bulker base *t*-BuOK/*t*-BuOH. The more crowded salt with leaving group P(*t*-Bu)$_3$ gives 85% of olefin in *t*-BuOK/*t*-BuOH and significant amount of styrene also in CH_3ONa/CH_3OH and C_2H_5ONa/C_2H_5OH. Intermediate values are obtained when the leaving groups are P(cyclohexyl)$_3$ and P(*n*-Bu)$_3$. The reactions of β-phenylethyltri-*n*-butylphosphonium bromide and β-phenylethyltricyclohexylphosphonium bromide with an excess of *t*-BuOK/*t*-BuOH (0.04 N to 0.12 N) at 30 °C followed good pseudo first order plot and the calculated rate constants, corrected for the % of olefin formed are $1.1 \cdot 10^{-2}$ lm^{-1}s^{-1} and $0.96 \cdot 10^{-2}$ lm^{-1}s^{-1} respectively.

Two possible mechanisms for styrene formation from these phosphonium salts are a concerted E2 mechanism [5] which is the mechanism operating with β-phenylethylammonium and sulphonium salts and halides [4] or an irreversible E1cb mechanism which would well explain the lack of leaving group effect. The α′-β-elimination mechanism [4] seems improbable, in fact, styrene is formed from β-phenylethyltriphenylphosphonium bromide and β-phenylethyltri-*t*-butylphosphonium bromide which cannot react by this mechanism. We think that more mechanistic studies are necessary in order to clarify the nature of this process.

Table. % Styrene formed in the basic decomposition of



R	Base/solvent	T[°C]	Styrene [%]	Ethylbenzene [%]
Phenyl[a]	OH^-/H_2O	74[d]	–	–
Phenyl[a]	EtONa/EtOH	74[d]	–	–
Phenyl[a]	*t*-BuOK/*t*-BuOH	74[d]	22.9	–
Cyclohexyl[b]	*t*-BuOK/*t*-BuOH	70[d]	32.5	–
Cyclohexyl[a]	*t*-BuOK/*t*-BuOH	30[c]	32.6	–
n-Bu[a]	EtONa/EtOH	74[d]	–	–
n-Bu[a]	*t*-BuOK/*t*-BuOH	74[c]	69.9	16.5
n-Bu[b]	*t*-BuOK/*t*-BuOH	30[d]	50.5	26.6
t-Bu[a]	CH_3ONa/CH_3OH	20[d]	45.7	–
t-Bu[a]	CH_3ONa/CH_3OH	55[d]	44.5	–
t-Bu[a]	EtONa/EtOH	20[d]	52.2	–
t-Bu[a]	EtONa/EtOH	55[d]	33.7	–
t-Bu[a]	*t*-BuOK/*t*-BuOH	70[d]	85.0	–

[a] Base concentration was 0.6–0.8 N; [b] base concentration was 0.1 N; [c] reaction time was 2 h; [d] reaction time was 15 h.

Experimental

Materials

Phosphonium salts were made by refluxing for 1 h in EtOH β-phenylethyl bromide with the corresponding phosphine. After dilution with anhydrous Et_2O the white solids were filtered and recrystallized (chloroform-ethylacetate). Br^- titration for all compounds gave the expected amount for 100% purity. Identification of compounds was also made by ^1H NMR spectroscopy. All the phosphines used were commercial materials.

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Determination of % styrene formed in the alkaline decomposition of β-phenylethylphosphonium salts

Styrene analyses were performed by vpc analysis with isopropyl benzene as standard (LAC 728 20% 3 m).

Kinetics measurements

Reagents were mixed in a cell thermostated at 30 °C of a Beckman DB–GT spectrophotometer and the increase in the absorbance of styrene at 250 nm was recorded.

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[5] In order to explain the lack of leaving group effect with this mechanism it should be assumed a very limited C–P bond breaking in the transition state.