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Mechanism of the Formation of Phenyltolylmethane by the Reaction of Toluene with Phosphorus Trichloride and Oxygen

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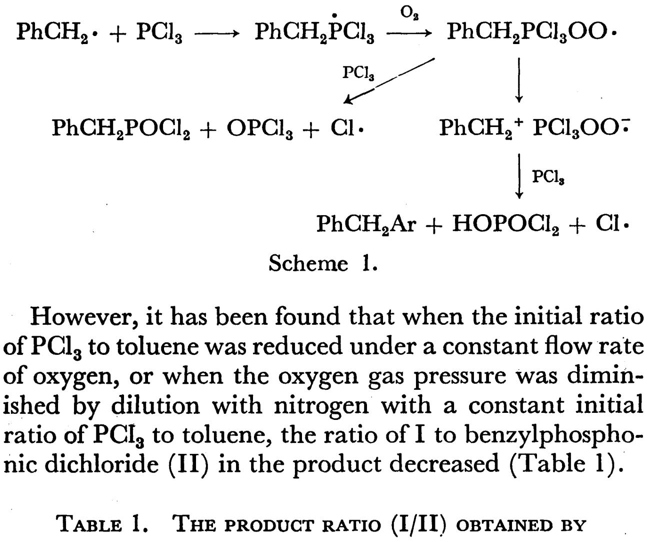
Synopsis. The formation of phenyltolylmethane by the reaction of toluene with PCl_3 and oxygen was shown to proceed by electrophilic attack on toluene by the benzyl cation, resulting from the decomposition of the trichlorobenzyloxyphosphoranyl peroxy radical ($PhCH_2OPCl_3OO\cdot$).

The formation of phenyltolylmethane (I) by the reaction of toluene with PCl_3 and oxygen was reported in a previous paper,[1] in which the mechanism of the formation was explained by the electrophilic attack on toluene by benzyl cation, resulting from the electron transfer from the benzyl radical to PCl_3 with the participation of oxygen as shown in Scheme 1.



Scheme 1.

However, it has been found that when the initial ratio of PCl_3 to toluene was reduced under a constant flow rate of oxygen, or when the oxygen gas pressure was diminished by dilution with nitrogen with a constant initial ratio of PCl_3 to toluene, the ratio of I to benzylphosphonic dichloride (II) in the product decreased (Table 1).

TABLE 1. THE PRODUCT RATIO (I/II) OBTAINED BY CHLOROPHOSPHONATION OF TOLUENE, CARRIED OUT UNDER SEVERAL CONDITIONS

Reactant ratio (Toluene/PCl_3)	Oxygen (%)	Time (h)	Yield (g)	Product ratio (I/II)
0.02	100	3	3.0	7
0.1	100	3	4.9	29
0.2	100	3	4.8	50
5	100	3	1.6	230
0.2	50	6	7.0	41
0.2	10	30	5.3	21

These results cannot be explained by Scheme 1, in which the benzyl radical reacts with PCl_3 exclusively to give a trichlorobenzylphosphranyl radical as an intermediate. It is well known that tervalent phosphorus compounds have high reactivities with free radicals, such as $RO\cdot$, $RS\cdot$, and methyl.[2] However, recently Dulog, Nielich, and Verhelst reported that resonance-stabilized radicals, such as $Ph_3C\cdot$, fail to react with PCl_3.[3] The reactivities of the free radical with PCl_3 decrease in the following order: $C_6H_5\cdot > t\text{-}C_5H_9\cdot > (CH_3)_2\dot{C}CN > (C_6H_5)_3C\cdot$. Bentrude also suggested that methyl and ethyl radicals react with $(C_6H_5)_2POR$, but that the more stable radicals, such as benzyl, do not appreciably react with $(C_6H_5)_2POR$,[4] because the ΔH_{PZ_4} for the reaction of $(C_6H_5)_2POR$ and benzyl radical (the enthalpy change of the formation of the phosphoranyl radical intermediate) is too small to form a phosphoranyl radical.[2,4] The ΔH_{PZ_4} is analyzed into three contributing terms: (1) the phosphorus orbital reorganization energy (ORE), (2) the strength of the bond to phosphorus being formed (ΔH_{PZ}), and (3) any resonance stability imparted to the phosphoranyl radical by the substituents on phosphorus (RE). Differences in the enthalpies of formation for strengths of the new bonds being formed and the resonance-stability difference (if ORE is assumed constant). The bond strength of benzyl is not known but is assumed to be considerably smaller than that for other free radicals, such as $RO\cdot$, $RS\cdot$, and methyl.[2] It is also supposed that PCl_3 may be less reactive than $(C_6H_5)_2POR$ because, in the former case, the effect of no resonance stability imparted to the phosphoranyl radical can be expected.

On the other hand, it is well known that the addition of oxygen to the radical is extremely fast and is probably diffusion controlled in many instances.[5] An extremely resonance-stabilized radical, such as $Ph_3C\cdot$, is very reactive with oxygen even though it is relatively inert with other species.[6]

Therefore, the benzyl radical may react preferentially with oxygen to form a benzyl peroxy radical (reaction 1) rather than with PCl_3 to form a trichlorobenzylphosphoranyl radical,

$$R\cdot \xrightarrow{O_2} ROO\cdot \quad (1)$$

$$R\cdot \xrightarrow[PCl_3]{} R\dot{P}Cl_3 \quad (2)$$

The benzyl peroxy radical is deoxygenated with PCl_3 to yield the benzyloxy radical (reaction 3),[3] which is trapped again with PCl_3 to form a trichlorobenzyloxyphosphoranyl radical (III),

$$ROO\cdot + PCl_3 \longrightarrow RO\cdot + POCl_3 \quad (3)$$

$$RO\cdot + PCl_3 \longrightarrow RO\dot{P}Cl_3 \text{ (III)} \quad (4)$$

Radical III reacts with oxygen to give a trichlorobenzyloxyphosphoranyl peroxy radical (IV), thus

$$RO\dot{P}Cl_3 + O_2 \longrightarrow ROPCl_3OO\cdot \text{ (IV)} \quad (5)$$

In the case of R≠benzyl, radical IV reacts with PCl_3 to give alkyl phosphorochloridate, $POCl_3$ and Cl.[7,8] However, when R has a lower ionization potential, such as for the benzyl radical (7.76 eV), the electron transfer from a benzyl group to an $OPCl_3OO$ group may occur to give an ionic structure such as IV′:

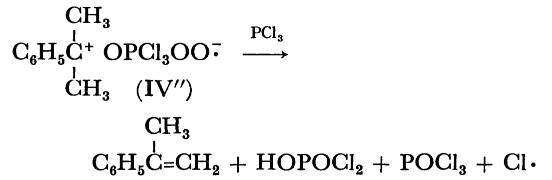
$$\mathrm{ROPCl_3OO\cdot} \longrightarrow \mathrm{R^+(OPCl_3OO\cdot)^-}\ (\mathrm{IV'}) \qquad (6)$$

The electrophilic attack of benzyl cation (IV′) on toluene gives phenyltolylmethane (I) as a final product, thus

$$\mathrm{IV'} + \mathrm{C_6H_5CH_3} \xrightarrow{\mathrm{PCl_3}} \mathrm{I} + \mathrm{HOPOCl_2} + \mathrm{POCl_3} + \mathrm{Cl\cdot} \qquad (7)$$

The formation of α-methylstyrene and its dimers by the chlorophosphonation of isopropylbenzene[1] can be explained in a similar manner.

But in this case, IV″ leads to α-methylstyrene by intramolecular proton-migration, thus



$$\mathrm{C_6H_5\overset{CH_3}{\underset{CH_3}{C^+}}\ OPCl_3OO^{\cdot-}}\ (\mathrm{IV''}) \xrightarrow{\mathrm{PCl_3}} \mathrm{C_6H_5\overset{CH_3}{C}{=}CH_2} + \mathrm{HOPOCl_2} + \mathrm{POCl_3} + \mathrm{Cl\cdot} \qquad (8)$$

The possibility of the direct formation of a benzyl cation from radical III (reaction 9) can be eliminated by the results that no α-methylstyrene and its dimers could be detected in the thermally-decomposed products of bis(α,α-dimethylbenzyl) peroxide in PCl_3 in a nitrogen atomsphere:

$$\mathrm{RO\dot{P}Cl_3}\ (\mathrm{III}) \longrightarrow \mathrm{R^+}\ \mathrm{O\dot{P}Cl_3^-} \qquad (9)$$

The remarkable formation of alkylphosphorodichloridate was observed in the chlorophosphonation of alkyl halide,[8] thus

$$\mathrm{ROPCl_3OO\cdot} + \mathrm{PCl_3} \longrightarrow \mathrm{ROPOCl_2} + \mathrm{POCl_3} + \mathrm{Cl\cdot} \qquad (10)$$

Therefore, there is another possilibity of the formation of a benzyl cation: the reaction *via* the heterolytic dissociation of the C–O bond of benzylphosphorodichloridate (V), thus

$$\mathrm{ROPOCl_2}\ (\mathrm{V}) \longrightarrow \mathrm{R^+}\ \mathrm{OPOCl_2^-} \qquad (11)$$

However, the possibility of this reaction can also be eliminated, because a mixture of dibenzylphosphorochloridate, toluene, PCl_3 and $POCl_3$ did not gave I in the presence of a trace of HCl at 0—5 °C.

Experimental

The general and detailed procedure was described in a previous paper.[1]

Chlorophosphonation. A mixture (130 ml) of the prescribed ratio of toluene/PCl_3 was placed in a reaction vessel. Oxygen or a mixture of oxygen and nitrogen gas was bubbled into the reaction mixture at a flow rate of 300 ml/min at a temperature of −15−0 °C. After the removal of a large portion of the unreacted materials and $POCl_3$, the residue was distilled *in vacuo*.[9] The I/II ratios were determined by glc analysis after treating the distillate with ethanol–triethylamine.

Thermal Decomposition of Bis(α,α-dimethylbenzyl) Peroxide in PCl_3. Bis(α,α-dimethylbenzyl) peroxide (0.1 mol) in PCl_3 (50 ml) was heated (70—80 °C) in a nitrogen atmosphere for a period of approximatately 6 h. The reaction mixture was poured into ice water and an oily layer was extracted with ether. No α-methylstyrene or its dimers were detected but a small amount of phenol was found by glc.

Reaction of Toluene with Dibenzylphosphorochloridate in the Presence of PCl_3, $POCl_3$, and HCl. The mixture of toluene (9.2 g, 0.1 mol), dibenzylphosphorochloridate (29 g, 0.1 mol), PCl_3 (24 g, 0.2 mol), $POCl_3$ (15 g, 0.1 mol) and a trace of HCl was stirred for a period of approximately 12 h at 0—5 °C. The mixture was poured into ice water. And oily layer was analyzed by glc. No. I was detected.

References

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9) A substantial amount of I was also detected by direct glc analysis on the undistilled and cooled (0 °C) reaction mixture, and on the oily product obtained after hydrolysis of the mixture with ice water.