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REACTION OF 1,3-DIPHENYL-TRIAZENE WITH TRIPHENYL-PHOSPHINE IN THE PRESENCE OF PERCHLORIC ACID: A SOURCE OF ARYL RADICALS

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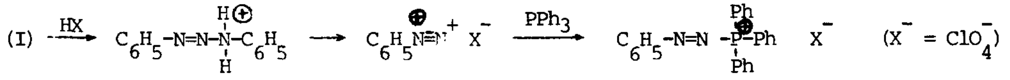
It has been shown that diaryltriazenes can react homolytically under several experimental conditions[1-4]. In this note we wish to report that 1,3-diphenyltriazene reacts at r.t. with PPh_3 in a number of aromatic solvents, in the presence of perchloric acid (72%), to give, among other products, an isomeric mixture of biaryls whose analysis unequivocally supports free radical aromatic substitution.

In a typical experiment a solution 2×10^{-3}M of 1,3-diphenyltriazene (I) and $HClO_4$ 72% (1 : 1 ratio) in monosubstituted benzenes (Table) was added to an equimolar amount of PPh_3, dissolved in the same solvents, at r.t. and under vigorous stirring. At the time evolution of nitrogen ceased (5hr.), a voluminous precipitate formed which was identified as N-aryl-hydrazino-triphenylphosphonium perchlorate (II) (30-35% yield)[5], (Calcd: N = 6.18; Found: N = 6.24); I.r.: ν(N-H) at 3100 cm^{-1} (broad) and a broad band at 1100 - 1000 cm^{-1} for (ClO_4^-); moreover (II) hydrolises quantitatively in EtOH to $(C_6H_5)_3P{=}0$ and $C_6H_5NH\text{-}NH_2$. The crude filtrate, analyzed by GLC, showed a mixture of ortho-, meta-, para-diphenyl isomers (0.2 gr.; 10%) (Table) together with $PPh_3P{=}0$ (10%) and a small amount of unidentified products. The yield of biaryls increased in a nitrogen atmosphere (12-14%) suggesting a homolytic mechanism in which oxygen acts as a radical scavenger[6]. Carrying out the reaction in homogeneous phase (DMSO/aromatic solvent), the yield increased to 17-19%.

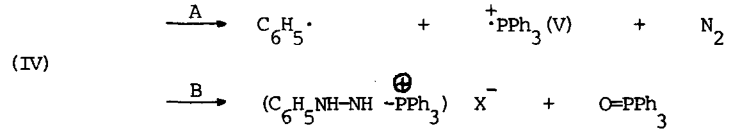
This reaction may be rationalized as follows:



$$\text{(I)} \xrightarrow{HX} C_6H_5\text{-N=N-}\overset{H\oplus}{\underset{H}{N}}\text{-}C_6H_5 \longrightarrow C_6H_5\overset{\oplus}{N}{\equiv}N^{+}\ X^{-} \xrightarrow{PPh_3} C_6H_5\text{-N=N-}\overset{Ph}{\underset{Ph}{\overset{\oplus}{P}}}\text{-Ph}\quad X^{-} \qquad (X^{-} = ClO_4^{-})$$

(III) (IV)

Intermediate (IV) may decompose either via A to aryl-radicals and a triphenylphosphonium cation radical (V) or via B to (II) and triphenyl-phosphine oxide



$$\text{(IV)} \begin{cases} \xrightarrow{A} C_6H_5\cdot \quad + \quad \overset{+}{\cdot}PPh_3\,(V) \quad + \quad N_2 \\ \xrightarrow{B} (C_6H_5NH\text{-}NH\text{-}\overset{\oplus}{P}Ph_3)\ X^{-} \quad + \quad O{=}PPh_3 \end{cases}$$

(II) (30-35%) (10%)

The aryl radical generated via A would give a homolytical aromatic substitution in monosubstituted benzenes to afford (o-,m-,p-) isomeric biphenyls. Free radical phenylation is also evidenced by the formation of bicumyl when the reaction was carried out in cumene.

TABLE

	Chlorobenzene				Anisole			
	K_T	%o-	%m-	%p-	K_T	%o-	%m-	%p-
Bz_2O_2[7]	1.40	50.0	32.0	18.0	2.00	70.0	17.0	16.0
dpt + $HClO_4$ + PPh_3	1.24	51.2	30.6	18.2	1.85	69.4	15.1	15.5
$PhN_2^+BF_4^-$ + PPh_3	1.20	49.8	29.6	20.6	1.90	68.2	16.0	15.8

dpt = diphenyltriazene ; K_T = total rate ratio.

As further evidence of the mechanism benzenediazonium tetrafluoborate and triphenylphosphine were allowed to react (in the ratio 1:1) in an aromatic medium yielding the same results (see Table).

It is noteworthy that aryl-diradical intermediates were suggested in homogeneous and heterogeneous phases in an aromatic medium[8,9]. On the other hand the aryl cation is considered to be the intermediate in aprotic polar solvents[10]. It has been also reported that aryl diazonium salts undergo homolytic decomposition in solution in DMSO of sodium nitrite[11] and CH_3OH[12]. It is therefore important that the presence of aryl radicals has been unambiguously demonstrated in a reaction, like ours, that proceeds at room temperature in a heterogeneous medium.

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