

## REACTION OF ARYLIDENECYANOACETAMIDES WITH *p*-TOLYL TETRACHLOROPHOSPHORANE

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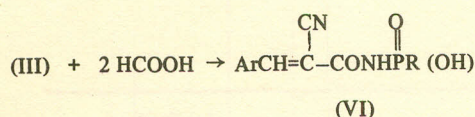
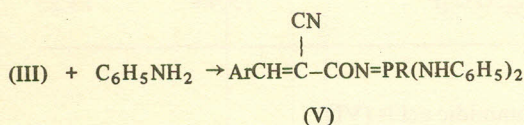
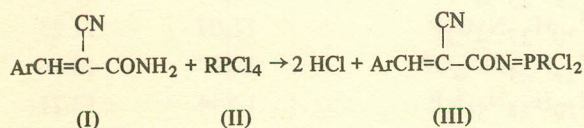
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Arylideneacyanoacetamides react with *p*-tolyltetrachloro-phosphorane in refluxing carbon tetrachloride to give N-(arylideneacyanoacetyl)*p*-tolyl phosphonimidic dichlorides. The structural assignments of the products were based on IR and chemical reactions.

### INTRODUCTION

In previous publications [1,2], we have described the reaction of arylideneacyanoacetamides (I) with phosphorus pentachloride and phenyltetrachlorophosphorane. In this work, the reaction of (I) with *p*-tolyltetrachlorophosphorane is investigated.

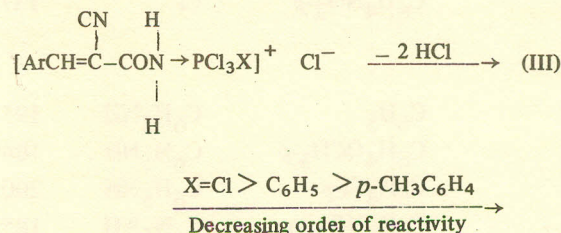
Thus, when arylideneacyanoacetamides (I) were refluxed with *p*-tolyltetrachlorophosphorane (II) in carbon tetrachloride, until the evolution of hydrogen chloride gas, ceased (ca., 1.5 hr.), they gave N-(arylideneacyanoacetyl)*p*-tolylphosphonimidic dichlorides (III)



- A, a = C<sub>6</sub>H<sub>5</sub>  
 b = C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-*p*  
 c = C<sub>6</sub>H<sub>4</sub>Cl-*p*  
 d = C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*m*  
 e = C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*p*  
 R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>

The presence of an electron-donating substituent in the aromatic nucleus of (II) has changed its reactivity towards

the cyanoacetamides (I) as compared with phosphorus pentachloride and phenyltetrachlorophosphorane (the required refluxing periods with (I) are 20 min and 30-60 min respectively). These results are consistent with the mechanism of the reaction [3], the first step of which is the formation of a heteropolar intermediate (IV) from which hydrogen chloride is eliminated leading to the products.



The structure of the products (III) was confirmed by IR spectroscopy and chemical reactions. The IR spectra of all the phosphonimidic dichlorides (III) display a band at 1280-1300 cm<sup>-1</sup> due to the P=N stretching vibration [4], with the concomitant disappearance of the NH stretching.

The dichlorides (II) condense with aniline to yield the dianilides (V). The P=N in (V) absorbs around 1320 cm<sup>-1</sup> i.e., with a shift to a higher frequency than in the starting dichlorides (III). The dichlorides (III) are sensitive to moisture. They react smoothly with two mole of anhydrous formic acid in dry benzene to yield N-(arylideneacyanoacetyl)*p*-tolylphosphonamidic acid (VI). The IR spectra of (VI) show a sharp band around 1250 cm<sup>-1</sup> attributed to P=O absorption [5].

### EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a Beckman IR-5A unit as KBr pellets. *p*-Tolylidi-

chlorophosphine[6] and arylidenecyanoacetamides[7] were prepared according to known procedures:

*Preparation of N-(arylideneacyanoacetyl)p-tolylphosphonimidic dichlorides (III).* A suspension of 0.01 mole of arylidenecyanoacetamides and 0.01 mole of *p*-tolyltetrachlorophosphorane in 50 ml carbon tetrachloride was refluxed until HCl evolution ceased, (ca., 1.5 hr.), during which complete dissolution of compounds occurred. The solution was cooled to room temperature and the precipitate

formed was collected and washed with carbon tetrachloride and crystallised from benzene or carbon tetrachloride. Yield 75-80%. (Table 1).

*Preparation of N-(arylideneacyanoacetyl)p-tolylphosphonimidic dianilides (V).* A solution of 4 mM aniline in 10 ml benzene was gradually added at room temperature to a suspension of the dichlorides (III), 1 mM in 30 ml benzene. The mixture was stirred at room temperature for 4 hr. and then refluxed 2 hr. The solid was filtered, dried,

Table - 1. N-(arylideneacyanoacetyl)p-tolylphosphorimidic dichlorides (III) and dianilides(V).

$$\text{ArCH}=\overset{\text{CN}}{\underset{|}{\text{C}}}-\text{CON}=\text{P}(\text{C}_6\text{H}_4\text{CH}_3=\text{p})\text{X}_2$$

Compound	Ar	X	Mp, °C	Formula	Analysis	
					Calcd. Cl	Found Cl
IIIa	C <sub>6</sub> H <sub>5</sub>	Cl	71	C <sub>17</sub> H <sub>13</sub> Cl <sub>2</sub> N <sub>2</sub> OP	19.50	19.40
b	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> -p	Cl	144	C <sub>18</sub> H <sub>15</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> P	18.07	18.27
c	C <sub>6</sub> H <sub>4</sub> Cl-p	Cl	142	C <sub>17</sub> H <sub>12</sub> Cl <sub>3</sub> N <sub>2</sub> OP	26.79	26.54
d	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -m	Cl	165	C <sub>17</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>3</sub> P	17.40	17.21
e	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -p	Cl	137	C <sub>17</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>3</sub> P	17.40	17.17
					%N	%N
Va	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> NH	195	C <sub>29</sub> H <sub>25</sub> N <sub>4</sub> OP	11.76	11.69
b	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> -p	C <sub>6</sub> H <sub>5</sub> NH	184	C <sub>30</sub> H <sub>27</sub> N <sub>4</sub> O <sub>2</sub> P	11.07	11.25
c	C <sub>6</sub> H <sub>4</sub> Cl-p	C <sub>6</sub> H <sub>5</sub> NH	200	C <sub>29</sub> H <sub>24</sub> ClN <sub>4</sub> OP	10.97	10.66
d	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -m	C <sub>6</sub> H <sub>5</sub> NH	185	C <sub>29</sub> H <sub>24</sub> N <sub>5</sub> O <sub>3</sub> P	13.44	13.21
e	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -p	C <sub>6</sub> H <sub>5</sub> NH	206	C <sub>29</sub> H <sub>24</sub> N <sub>5</sub> O <sub>3</sub> P	13.44	13.23

Table - 2. N-arylideneacyanoacetyl)p-tolylphosphoramidic acids (VI)

$$\text{ArCH}=\overset{\text{CN}}{\underset{|}{\text{C}}}-\overset{\text{O}}{\parallel}{\text{C}}\text{ONHP}(\text{C}_6\text{H}_4\text{CH}_3=\text{p})(\text{OH})$$

Compound	Ar	M.p., °C	Formula	Analysis	
				Calcd. %N	Found %N
VIa	C <sub>6</sub> H <sub>5</sub>	108	C <sub>17</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub> P	8.59	8.79
b	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> -p	205	C <sub>18</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub> P	7.86	7.66
c	C <sub>6</sub> H <sub>4</sub> Cl-p	199	C <sub>17</sub> H <sub>14</sub> ClN <sub>2</sub> O <sub>3</sub> P	7.77	7.56
d	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -m	124	C <sub>17</sub> H <sub>14</sub> N <sub>3</sub> O <sub>5</sub> P	11.32	11.44
e	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> -p	209	C <sub>17</sub> H <sub>14</sub> N <sub>3</sub> O <sub>5</sub> P	11.32	11.57

washed well with water, dil. HCl, water and then crystallised from ethanol in colorless needles. Yield 80-90 % (Table 1).

*Preparation of N-(arylideneacyloacetyl)p-tolylphosphonamidic acids (VI).* A solution of 0.01 mole of the dichlorides (III) in dry benzene was treated with 0.02 mole of anhydrous formic acid. The mixture kept at room temperature for 4 hr. and then refluxed 2 hr. The precipitated solid was collected and crystallised from ethanol. Yield 60-70%. (Table 2).

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