

## SOME PRODUCTS OF THE REACTION OF PHENYLHYDRAZONES AND PHOSPHORUS TRICHLORIDE

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It is found that reaction of phosphorus trichloride with the phenylhydrazones of acetone, methylethyl, methylpropyl and methylbutyl ketones are compounds with one atom of phosphorus to one phenylhydrazone group. They do not contain chlorine, and distill without decomposition under vacuum. The view is advanced that they have structure I. A similar compound was also obtained by the reaction of phosphorus trichloride with acetaldehyde.

It is known that the reaction of phenylhydrazine with chlorides of phosphorus acids gives  $\beta$ -phenylhydrazides [1-3], a series which has insecticidal properties, and has been patented for combating harmful insects [4, 5]. The corresponding arylhydrazine derivatives, with a acyl radicals on the same nitrogen atom, as the aromatic group, are not described in the literature.

In connection with a study of the relationship between structure and pesticidal properties, it was of interest to synthesize and investigate such a series of compounds. First of all investigation of the reaction of phenylhydrazones with phosphorus trichloride was undertaken.

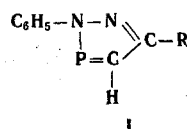
The reaction of phosphorus trichloride with the phenylhydrazones of acetone, methylethyl-, methylpropyl-, and methylbutyl ketones gives liquid products containing one phosphorus atom per molecule of phenylhydrazone taken, and not containing chlorine.

Analyses and molecular weight determinations of the resultant compound confirm the structure proposed for the molecule.

A more detailed study has been made of the properties of the product of reaction of phosphorus trichloride with acetone phenylhydrazone. It is stable up to 250° when moisture and air are excluded, and does not react with sulfur, ammonia, amines, alkyl halides, magnesium, sodium, ketones, and aromatic aldehydes,

but it forms a complex with cuprous iodide, a hydrochloride with dry hydrogen chloride, and bromine converts it to a dibromide in which the phosphorus remains trivalent. Alkaline hydrolysis converts it to acetone phenylhydrazone, while boiling with ethanol gives triethyl phosphite and acetone phenylhydrazone.

Hence it can be assumed that formula I represents the structure of the reaction products from phenylhydrazones of ketones.



a R=CH<sub>3</sub>; b R=C<sub>2</sub>H<sub>5</sub>; c R=C<sub>3</sub>H<sub>7</sub>;  
d R=C<sub>4</sub>H<sub>9</sub>; e R=H

## EXPERIMENTAL

**Reaction of phosphorus trichloride with phenylhydrazones.** All the reactions, including the working up of reaction products were carried out in a current of dry nitrogen.

a) 1 mole Phenylhydrazone in 3 volumes of ether was added over a period of 3 hr, to a solution of 3 moles freshly-distilled phosphorus trichloride in 3 volumes of dry ether which was stirred and cooled to 0° C. The products were left overnight and filtered, the solid washed with dry ether, the ether solutions combined and evaporated, then the residue vacuum distilled.

b) Using Et<sub>3</sub>N as the HCl acceptor, the reaction was run under the same conditions, using the following proportions of reactants: 1.25 mole PCl<sub>3</sub>, 1 mole phenylhydrazone, and 3.75 mole Et<sub>3</sub>N. The table gives the results of the experiments.

The products were greenish-yellow mobile liquids with a slight odor of phosphines.

**Chemical reactions of Ia.** a) Cu<sub>2</sub>I<sub>2</sub> complex. 5 g (0.013 mole) freshly prepared Cu<sub>2</sub>I<sub>2</sub> was added to 6.28 g (0.035 mole) Ia, the mixture left for 2 days, then extracted with methylene chloride, the extract evaporated, and the starting Ia distilled off under a pressure

Reaction Products from Phosphorus Trichloride and Phenylhydrazone Ketones

Compound	Bp, °C (pressure, mm)	d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	Molecular weight		Formula	Found, %			Calculated, %			Yield, %
				Found	Calculated		C	H	P	C	H	P	
Ia	73 (0.05)	1.3004	1.6290	172 184	176.16	C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> P	61.36 60.97	4.98 5.27	17.25 17.03	61.36	5.15	17.58	54
Ib	101 (0.07)	1.1218	1.6220	202 208	190.20	C <sub>10</sub> H <sub>11</sub> N <sub>2</sub> P*	63.48 63.53	6.50 6.26	16.00 15.99	63.15	5.83	16.28	53
Ic	103 (0.09)	1.0976	1.6015	207 211	204.21	C <sub>11</sub> H <sub>13</sub> N <sub>2</sub> P	64.66 65.04	6.32 6.57	15.02 15.29	64.70	6.42	15.17	96
Id	114 (0.06)	1.0669	1.5918	218 223	218.24	C <sub>12</sub> H <sub>15</sub> N <sub>2</sub> P	66.32 66.14	7.62 7.52	13.52 14.01	66.04	6.93	14.19	49
Ie	85-87 (0.2)	1.1811	1.6450	—	—	C <sub>9</sub> H <sub>7</sub> N <sub>2</sub> P	59.12 59.53	4.47 4.87	18.78 18.44	59.26	4.35	19.11	10

\*found: N 14.51; 14.28%, calculated: N 14.73%.

of 0.08 mm, bath temperature 120°C. The  $Cu_2I_2$  complex with **Ia** was precipitated from the residue with ether, yield 0.9 g of a light yellow powder. Found: P 8.70%, calculated for  $C_9H_9N_2P \cdot CuI$ : P 8.45%.

b) Reaction with hydrogen chloride. Dry HCl gas was passed into 14.5 g (0.084 mole) **Ia**, with water cooling, until constant weight was reached. After 2 days the crystals were filtered off and washed with petrol ether and ether, yield 4.4 g hydrochloride of **Ia**, as white crystals, mp 90°C, which fell to powder in air. Found: P 15%; P 14.45; Cl 16.55%, calculated for  $C_9H_9N_2P \cdot HCl$ : P 14.56; Cl 16.68%.

c) Reaction with ethanol. 7.9 g (0.045 mole) **Ia** was refluxed for 5 hr with excess absolute EtOH, the ethanol distilled off, and the residue vacuum distilled, to give 3 g triethylphosphite 36°C (6 mm),  $n_D^{20}$  1.4090. It was identified as its  $Cu_2I_2$  complex, mp 110.8°C\*. Found: P 8.92%, calculated: P 8.69%.

e) Alkaline hydrolysis. 5 ml Water was gradually added to 6.5 g (0.037 mole) **Ia**, followed by a solution of 6.8 g KOH in 10 ml water. The oily layer was isolated, extracted with ether, and the extracts distilled to give 2.5 g (0.017 mole) acetone phenylhydrazone bp 120°C (8 mm),  $n_D^{21}$  1.5872.

\* The literature gives [6] mp 110°-111°C.

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