ADDITION OF DIALKYL PHOSPHOROUS ACIDS TO 3,3$'$-DIMETHOXY-DIPHENYL-4,4$'$- AND DIPHENYLMETHANE-4,4$'$-DIISOCYANATES

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Abstract

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ADDITION OF DIALKYL PHOSPHOROUS ACIDS TO 3,3′-DIMETHOXY-DIPHENYL-4,4′- AND DIPHENYLMETHANE-4,4′-DIISOCYANATES

(Presented by Academician B. A. Arbuzov, 26 VI 1961)

We have previously shown that dialkyl phosphorous acids, in the presence of sodium alcoholate, readily add to 1,5-naphthylene-, 1,6-hexamethylene-, and 2,4-toluylene diisocyanates ([1–2]). Continuing investigations in this direction, we decided to study the addition of dialkyl phosphorous acids to 3,3′-dimethoxy-diphenyl-4,4′- and diphenylmethane-4,4′-diisocyanates.

It was found that dialkyl phosphorous acids, in the presence of a small amount of sodium, also add readily to these diisocyanates. In general form, the interaction of diisocyanates with dialkyl phosphorous acids can be represented by the following equation:

$$(RO)_2POH + Na \rightarrow (RO)_2PONa$$

$$R\begin{matrix}N=C=O\\N=C=O\end{matrix} + (RO)_2POH \xrightarrow{(RO)_2PONa} R\begin{matrix}N=C-OHO=P(OR)_2\\N=C=O\qquad\quad|\end{matrix} +$$

$$+ (RO)_2POH \xrightarrow{(RO)_2PONa} R\begin{matrix}N=C-OH\\N=C-OH\end{matrix}\begin{matrix}O=P(OR)_2\\|\\|\\O=P(OR)_2\end{matrix} \rightleftarrows R\begin{matrix}NHCOP\ (OR)_2\\NHCOP\ (OR)_2\end{matrix}$$

The mechanism of this reaction is analogous to the mechanism of the interaction of dialkyl phosphorous acids, in the presence of sodium alcoholates, with 1,5-naphthylene diisocyanate.

The equilibrium is strongly shifted toward formation of the ketone form ([3]). Thus, for example, by the action of sodium ethoxide on a benzene solution of the 3,3′-dimethoxy-4,4′-diphenyl bis-diethyl ester of amidophosphonuravic acid, the sodium derivative was obtained according to the scheme:

$$(C_2H_5O)_2POCONH\ C_6H_3(OCH_3) - C_6H_3(OCH_3)\ NHCOP\ (OC_2H_5)_2 + 2C_2H_5ONa \rightarrow$$

$$\rightarrow (C_2H_5O)_2POCONNa\ C_6H_3(OCH_3) - C_6H_3(OCH_3)\ NCOP\ (OC_2H_5)_2Na + 2C_2H_5OH.$$

In this case the addition product reacts with sodium ethoxide in the ketone form. Studies in this direction are continuing. All the synthesized substances crystallize on prolonged standing, with the exception of products Nos. 9-12 (Table 1).

Table 1

$$(RO)_2POCONH\ \langle\langle C_6H_4\rangle\rangle - CH_2 - \langle\langle C_6H_4\rangle\rangle NHCOP(O)(OR)_2$$

No.	R	m.p.,* °C	Phosphorus content, %, found	Phosphorus content, %, calculated	Nitrogen content, %, found	Nitrogen content, %, calculated	Yield, %	Empirical formula
1	CH_3	155-156	12.92	12.80	13.19	5.74	5.70	5.95	70	$C_{19}H_{24}O_8N_2P_2$
2	C_2H_5	115-116	11.40	11.45	11.78	5.21	5.18	5.32	76	$C_{23}H_{32}O_8N_2P_2$
3	*n*-C_3H_7	88-89	10.53	10.50	10.65	4.67	4.57	4.81	83	$C_{27}H_{40}O_8N_2P_2$

No.	R	m.p.,* °C	Phosphorus content, %, found	Phosphorus content, %, calculated	Nitrogen content, %, found	Nitrogen content, %, calculated	Yield, %	Empirical formula
4	*iso*-C_3H_7	178–179, with considerable decomposition	10.62	10.45	10.65	4.70	4.81	88	$C_{27}H_{40}O_8N_2P_2$
5	*n*-C_4H_9	68–70	9.49	9.38	9.71	4.19	4.38	66	$C_{31}H_{48}O_8N_2P_2$
6	*iso*-C_4H_9	102–103	9.51	9.37	9.71	4.09	4.38	84	$C_{31}H_{48}O_8N_2P_2$
7	$ClCH_2CH_2$	111–113	9.04	9.00	9.33	3.96	4.08	85	$C_{23}H_{28}O_8N_2P_2Cl_4$

$(RO)_2POCONH\langle\langle C_6H_3(OCH_3)\rangle\rangle - \langle\langle C_6H_3(OCH_3)\rangle\rangle NHCOP(O)(OR)_2$

No.	R	m.p.,* °C	Phosphorus content, %, found	Phosphorus content, %, calculated	Nitrogen content, %, found	Nitrogen content, %, calculated	Yield, %	Empirical formula
8	CH_3	102–104	11.77	11.86	12.01	5.12	5.42	62	$C_{20}H_{26}O_{10}N_2P_2$
9	C_2H_5	148–150	10.38	10.49	10.83	4.45	4.89	68	$C_{24}H_{34}O_{10}N_2P_2$
10	*iso*-C_3H_7	146	9.76	9.70	9.86	4.45	4.45	79	$C_{28}H_{42}O_{10}N_2P_2$
11	*iso*-C_4H_9	125–126	8.92	8.64	9.06	3.93	4.09	84	$C_{32}H_{50}O_{10}N_2P_2$
12	$ClCH_2CH_2$	127–128	8.37	8.33	8.73	3.61	3.94	86	$C_{24}H_{30}O_{10}N_2P_2Cl_4$

* The melting point was determined in sealed capillaries.

They were purified by twofold recrystallization at low temperature from methyl alcohol. These are white crystalline substances, readily soluble in alcohol, benzene, dioxane, acetone, etc. They are insoluble in water. The properties of the addition products are presented in Table 1.

Thus, the addition of dialkyl phosphorous acids to 3,3′-dimethoxy-diphenyl-4,4′- and diphenylmethane-4,4′-diisocyanates has been studied.

In conclusion, we consider it our duty to express our gratitude to B. M. Tsi-gin for kindly providing the diisocyanates for our investigations.

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Note: Figure translations are in progress. See original paper for figures.