

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

1961

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**Abstract**

**Full Text**

**CHEMISTRY**

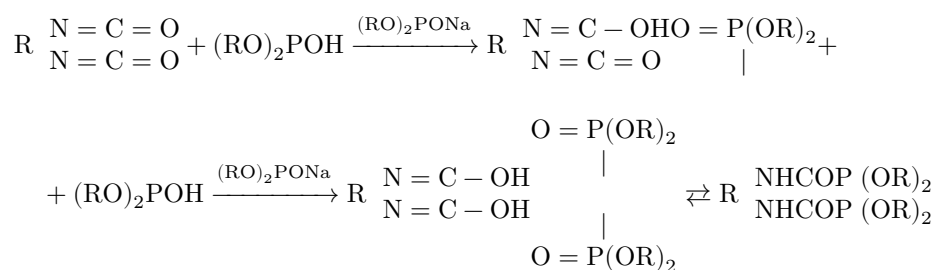
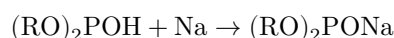
**E. V. KUZNETSOV and M. I. BAKHITOV**

**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)*

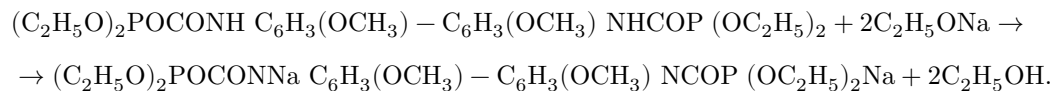
We have previously shown that dialkyl phosphorous acids, in the presence of sodium alcoholate, readily add to 1,5-naphthylene-, 1,6-hexamethylene-, and 2,4-toluylene diisocyanates (<sup>1-2</sup>). Continuing investigations in this direction, we decided to study the addition of dialkyl phosphorous acids 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:



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.

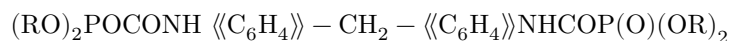
The equilibrium is strongly shifted toward formation of the ketone form (<sup>3</sup>). Thus, for example, by the action of sodium ethoxide on a benzene solution of the 3,3'-dimethoxy-4,4'-diphenyl bis-diethyl ester of amidophosphonuravic acid, the sodium derivative was obtained according to the scheme:



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).

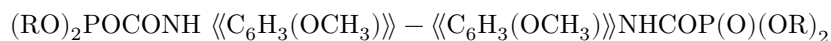
**Table 1**

No.	R	m.p.,* °C	Phosphorus		Nitrogen		Yield, %	Empirical for- mula
			Phosphorus con- tent, %, found	Phosphorus con- tent, %, calcu- lated	Nitrogen con- tent, %, found	Nitrogen con- tent, %, calcu- lated		



No.	R	m.p.,* °C	Phosphorus		Nitrogen		Yield, %	Empirical for- mula	
			Phosphorus con- tent, %, found	Phosphorus con- tent, %, calcu- lated	Nitrogen con- tent, %, found	Nitrogen con- tent, %, calcu- lated			
1	CH <sub>3</sub>	155- 156	12.92	12.80	13.19	5.74	5.70	70	C <sub>19</sub> H <sub>24</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
2	C <sub>2</sub> H <sub>5</sub>	115- 116	11.40	11.45	11.78	5.21	5.18	76	C <sub>23</sub> H <sub>32</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
3	<i>n</i> - C <sub>3</sub> H <sub>7</sub>	88-89	10.53	10.50	10.65	4.67	4.57	83	C <sub>27</sub> H <sub>40</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>

No.	R	m.p.,* °C	Phosphorus		Nitrogen		Yield, %	Empirical for- mula		
			Phosphorus con- tent, %, found	content, %, calcu- lated	Nitrogen con- tent, %, found	con- tent, %, calcu- lated				
4	<i>iso</i> - C <sub>3</sub> H <sub>7</sub>	178- 179, with considerable de- com- posi- tion	10.62	10.45	10.65	4.70	4.68	4.81	88	C <sub>27</sub> H <sub>40</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
5	<i>n</i> - C <sub>4</sub> H <sub>9</sub>	68-70	9.49	9.38	9.71	4.19	4.23	4.38	66	C <sub>31</sub> H <sub>48</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
6	<i>iso</i> - C <sub>4</sub> H <sub>9</sub>	102- 103	9.51	9.37	9.71	4.09	4.13	4.38	84	C <sub>31</sub> H <sub>48</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub>
7	ClCH <sub>2</sub> CH <sub>2</sub>	111- 113	9.04	9.00	9.33	3.96	4.08	4.21	85	C <sub>23</sub> H <sub>28</sub> O <sub>8</sub> N <sub>2</sub> P <sub>2</sub> Cl <sub>4</sub>



No.	R	m.p.,* °C	Phosphorus		Nitrogen		Yield, %	Empirical for- mula		
			Phosphorus con- tent, %, found	content, %, calcu- lated	Nitrogen con- tent, %, found	con- tent, %, calcu- lated				
8	CH <sub>3</sub>	102- 104	11.77	11.86	12.01	5.12	5.09	5.42	62	C <sub>20</sub> H <sub>26</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub>
9	C <sub>2</sub> H <sub>5</sub>	148- 150	10.38	10.49	10.83	4.45	4.67	4.89	68	C <sub>24</sub> H <sub>34</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub>
10	<i>iso</i> - C <sub>3</sub> H <sub>7</sub>	146	9.76	9.70	9.86	4.45	4.27	4.45	79	C <sub>28</sub> H <sub>42</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub>
11	<i>iso</i> - C <sub>4</sub> H <sub>9</sub>	125- 126	8.92	8.64	9.06	3.93	3.86	4.09	84	C <sub>32</sub> H <sub>50</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub>
12	ClCH <sub>2</sub> CH <sub>2</sub>	127- 128	8.37	8.33	8.73	3.61	3.48	3.94	86	C <sub>24</sub> H <sub>30</sub> O <sub>10</sub> N <sub>2</sub> P <sub>2</sub> Cl <sub>4</sub>

\* 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.

Kazan Chemical-Technological Institute  
named after S. M. Kirov

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20 VI 1961

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

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