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Abstract

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ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO 1,5-NAPHTHYLENE DIISOCYANATE

(Presented by Academician B. A. Arbuzov, 23 V 1960)

It is known that dialkylphosphorous acids readily add to substances containing carbon-oxygen, carbon-nitrogen, and unsaturated carbon-carbon bonds, with the formation of various phosphorus-containing compounds.

Dialkylphosphorous acids, reacting with esters of isocyanic acid ($^{1-3}$), give dialkyl esters of amidophosphonuric acid.

It was of interest to study the addition of dialkylphosphorous acids to diisocyanates. In the present work it is shown that dialkylphosphorous acids readily add to 1,5-naphthylene diisocyanate. The addition reaction may be represented by the following scheme:

$$(\mathrm{RO})_2\mathrm{POH} + \mathrm{RONa} \rightleftharpoons (\mathrm{RO})_2\mathrm{PONa} + \mathrm{ROH}$$

$$\text{1,5-naphthylene diisocyanate} + (\mathrm{RO})_2\mathrm{PONa} \longrightarrow \text{sodium salt of the addition product} \qquad (I)$$

$$\text{sodium salt of the addition product} + (\mathrm{RO})_2\mathrm{POH} \longrightarrow \text{enolic product} + (\mathrm{RO})_2\mathrm{PONa} \longrightarrow \text{5-naphthylene isocya}$$

$$\text{5-naphthylene isocyanate-1-dialkyl ester of amidophosphonuric acid} + (\mathrm{RO})_2\mathrm{POH} \xrightarrow{(\mathrm{RO})_2\mathrm{PONa}} \text{naphthylene-1,5}$$

where $R = \mathrm{CH}_3$; $\mathrm{C}_2\mathrm{H}_5$; n-$\mathrm{C}_3\mathrm{H}_7$; iso-$\mathrm{C}_3\mathrm{H}_7$; n-$\mathrm{C}_4\mathrm{H}_9$; iso-$\mathrm{C}_4\mathrm{H}_9$, iso-$\mathrm{C}_5\mathrm{H}_{11}$; $\mathrm{CH}_2{=}\mathrm{CH}{-}\mathrm{CH}_2$.

A possible mechanism of the transformations is that initially sodium alkoxide enters into an exchange reaction with dialkylphosphorous acid. Then the resulting Na salt of dialkylphosphorous acid in the enolic form reacts with one carbonyl group of the isocyanate group of the diisocyanate molecule. In this process, an intermediate product I is first formed. This product reacts with dialkylphosphorous acid to form product II, 5-naphthylene isocyanate-1-dialkyl ester of amidophosphonuric acid.

Then, according to the same scheme, the second NCO group reacts, with formation of naphthylene-1,5-bis-dialkyl ester of amidophosphonuric acid.

The reaction proceeds in chlorobenzene with brief heating on a water bath. The addition products are white crystalline substances, soluble in acetone, alcohol, dioxane, etc. The properties of these products are presented in Table 1.

To prove the structure of the obtained addition products, one of them—naphthylene-1,5-bis-di-*n*-butyl ester of amidophosphonoformic acid—was obtained by A. E. Arbuzov' s method from naphthylene-1,5-bis-carbamoyl chloride and tri-*n*-butyl phosphite. A mixed melting-point test showed no depression.

Table 1

Formula	Solvent from which recrystallized	m.p., °C	Phosphorus content, % found	Phosphorus content, % calculated	Yield, %
Naphthalene-1,5-bis$NHC(O)PO(OCH_3)_2$	Acetone	185 with decomposition	14.7	14.4	80
Naphthalene-1,5-bis$NHC(O)PO(OC_2H_5)_2$	Acetone, alcohol	186–187 with decomposition	12.77	12.76	85.7
Naphthalene-1,5-bis$NHC(O)PO(OC_3H_7-*n*)_2$	Acetone, alcohol	186 with decomposition	11.32	11.65	87
Naphthalene-1,5-bis$NHC(O)PO(OC_3H_7-*iso*)_2$	Acetone, alcohol	184–185 with decomposition	11.37	11.65	85
Naphthalene-1,5-bis$NHC(O)PO(OC_4H_9-*n*)_2$	Alcohol, dioxane	183–184 with decomposition	9.8	10.36	84
Naphthalene-1,5-bis$NHC(O)PO(OC_4H_9-*iso*)_2$	Alcohol, dioxane	180–181	10.36	10.36	89

Formula	Solvent from which recrystallized	m.p., °C	Phosphorus content, % found	Phosphorus content, % calculated	Yield, %
Naphthalene-1,5-bis$NHC(O)PO(OC_5H_{11}-*iso*)_2$	Alcohol, acetone	174-175	8.96	9.48	90
Naphthalene-1,5-bis$NHC(O)PO(OCH_2—CH=CH_2)_2$	Alcohol	157-159	11.14	11.6	95

Thus, an easily occurring reaction of dialkylphosphorous acids with diisocyanates has been found.

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