ISOCYANATES OF THE QUINOLINE SERIES

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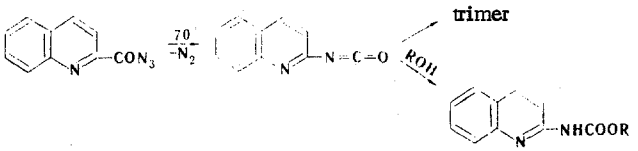
The isocyanates obtained by rearrangement of azides of quinaldic and quinoline-2,4-dicarboxylic acids exist as trimers. A number of urethanes were obtained by the decomposition of these azides in the presence of alcohols. The possibility of the use of the azide of quinoline-2,4-carboxylic acid to obtain polymers was investigated.

Isocyanates of the heterocyclic series are currently being studied in connection with the possibility of their use for the synthesis of pharmaceutical preparations [1-3] and high-molecular-weight compounds [4,5].

In this communication, we describe the synthesis and several transformations of isocyanates of the quinoline series. 2-Quinolyl isocyanate and 2,4-quinolyl diisocyanate were obtained by rearrangement of the azides of quinaldic (I) and quinoline-2,4-dicarboxylic (II) acids via the Curtius method by heating in dry benzene to 60-70°C. Trimerization to triquinolyl isocyanurates occurs under the reaction conditions. The characteristic frequencies of the N=C=O group (2200-2270 cm^{-1}) are absent in the IR spectra of the trimers, and there is a C=O band at 1715 cm^{-1}. The trimers of the isocyanates are stable on heating and do not change on refluxing with water, alcohols, and alkalis. A number of urethanes were obtained by heating I or II with alcohols, and polymers of the polyurethane type with molecular weights of 12,000-14,000 and polyureas with molecular weights of 8000-10,000 are formed when II is decomposed in the presence of ethylene glycol or hexamethylenediamine.



EXPERIMENTAL

Quinaldic Acid Azide (I). A solution of 3.5 g (0.05 mole) of sodium nitrite in 20 ml of water was added to a cooled (to 10°) solution of 4.7 g (0.025 mole) of quinaldic acid hydrazide in 90 ml of 2% hydro-

TABLE 1. Alkoxycarbonylaminoquinolines

Compound	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	N	C	H	N	
2-(Ethoxycarbonylamino)quinoline	98	$C_{12}H_{12}N_2O_2$	66,4	5,8	19,3	66,7	5,5	19,4	80
2-(Isopropoxycarbonylamino)-quinoline	92	$C_{13}H_{14}N_2O_2$	68,0	6,0	12,5	67,8	6,1	12,1	85
2-(Allyloxycarbonylamino)quinoline	72—73	$C_{13}H_{12}N_2O_2$	68,2	5,7	12,4	68,4	5,7	12,3	92
2-(Benzyloxycarbonylamino)quinoline	98	$C_{17}H_{14}N_2O_2$	73,5	5,2	10,3	73,4	5,0	10,1	80
2,4-Di(ethoxycarbonylamino)-quinoline	180	$C_{15}H_{17}N_3O_4$	59,7	5,8	13,6	59,4	5,6	13,9	87

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chloric acid. The resulting precipitate was removed by filtration, washed with cold water, and air-dried to give 4.5 g (90%) of a product with mp 93°. Found: C 60.8; H 3.2; N 28.3%. $C_{10}H_6N_4O$. Calculated: C 60.6; H 3.0; N 28.3%.

Quinoline-2,4-dicarboxylic Acid Diazide (II). Similarly, 4.8 g (90%) of II with mp 82° was obtained from 4.9 g (0.02 mole) of quinoline-2,4-dicarboxylic acid dihydrazide, dissolved in 150 ml of 2% hydrochloric acid, and 5.6 g (0.04 mole) of sodium nitrite in 40 ml of water. Found: C 49.6; H 2.0; N 36.8%. $C_{11}H_5N_7O_2$. Calculated: C 49.4; H 1.8; N 36.7%.

Triquinolyl Isocyanurate. A suspension of 5 g (0.025 mole) of I in 50 ml of dry benzene was heated to 60-70°. After the solid had dissolved, the solution was cooled, and the resulting precipitate was recrystallized from benzene to give 3.8 g (89%) of a product with mp 216°. Found: C 70.4; H 3.7; N 16.5%; M 500 (ebullioscopically in dioxane). $C_{30}H_{18}N_6O_3$. Calculated: C 70.6; H 3.5; N 16.5%; M 510.

Alkoxycarbonylaminoquinolines. These compounds were obtained by heating I or II in excess alcohol at 80° for 1 h. The precipitate that formed on cooling was recrystallized from n-heptane (Table 1).

Decomposition of II in Ethylene Glycol. A solution of 2.67 g (0.01 mole) of II and 1.2 g (0.02 mole) of ethylene glycol in 50 ml of dioxane was heated to 60-80° under an inert gas. The precipitated polymer was removed by filtration, washed with alcohol, and vacuum-dried to give a quantitative yield of a polymer with mp 240-247° and a molecular weight of 12,100; 14,300 (via the method in [6]).

Decomposition of II in Hexamethylenediamine. As in the preceding experiment, 4.7 g (95%) of a polymer with mp 210-214° and a molecular weight of 10,100; 8300 was obtained from 2.67 g (0.01 mole) of II and 2.9 g (0.025 mole) of hexamethylenediamine.

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