SIDE REACTIONS IN SYNTHESIS OF PHENYL CYANATE BY ACYLATION OF PHENOL WITH CYANOGEN HALIDES

UDC 542,91,002.67:547.551.43

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Aryl cyanates are easily cyclotrimerized to triaryl cyanurates [1], in which connection the catalysts can be phenols and tertiary amines, the starting products in the synthesis of acyl cyanates by the acylation of phenols with cyanogen halides. This creates difficulties in purifying the aryl cyanates, especially when purification is by fractional distillation in vacuo.

The acylating agent can be ClCN [1], as well as BrCN [2], but we were unable to obtain the pure phenyl cyanate (PC) when BrCN was used. Employing GLC, it was shown by us that the competing von Braun reaction [3, 4] takes place in the given case with the formation of diethylcyanamide (I)

 $\begin{array}{l} BrCN + N(C_2H_5)_3 \xrightarrow{O^*} N \equiv C - N(C_2H_5)_2 + C_2H_5Br \\ (I) \end{array}$

In the synthesis of PC this reaction leads to upsetting the stoichiometric ratios of the starting compounds and the free phenol remains in the end product, which makes the purification of the formed PC difficult in that it causes its cyclotrimerization during vacuum-distillation or during storage.

When CICN in used the similar competing reaction proceeds to less degree than with BrCN. Thus, only traces of (I) were detected in the distilled PC when an equimolar ratio of the starting components was reacted. Upsetting the equimolarity (1.2-1.3 mole of CICN per mole of phenol) leads to an increase (up to 13-15%) in the amount of (I) in the reaction product. The presence of (I) in the distilled PC was confirmed by the identification of its GLC and IR spectra with those of a specimen obtained by counter synthesis.

Phenyl cyanate and (I) have close boiling points, which makes their separation by fractional distillation difficult. It is interesting that (I) is not an active cyclotrimerization catalyst and the formation of triphenyl cyanurate is not observed when PC, contaminated with (I), is stored for a long time (in the absence of other, more active impurities).

EXPERIMENTAL METHOD

The IR spectra in the 4000-250 cm⁻¹ region were recorded on a Perkin-Elmer 457 IR spectrometer equipped with a diffraction lattice. The samples were prepared as a thin layer between salt windows.

For the GLC we used a glass column (2.5 m) filled with 3% of stationary phase XE-60, deposited on Chromosorb W (80-100 mesh), at 140°C, and a carrier-gas flow rate of 40 ml/min.

Phenyl cyanate [1] was obtained by the acylation of phenol with cyanogen chloride in the presence of triethylamine; bp 42° (1 mm).

Diethylcyanamide (I). To a mixture of 40 ml of water and 10 g of ice was added 0.2 mole of CaNCN. After the gradual addition of 0.4 mole of 40% NaOH solution in 30 min at $\leq 25^{\circ}$ the mixture was kept at 20° for 1 h. Then 0.4 mole of C_2H_5Br in 50 ml of alcohol was added and the mixture was kept at gentle reflux for 6 h. The precipitate was filtered, the unreacted C_2H_5Br was distilled from the mother liquor and the

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp.1414-1415, June, 1974. Original article submitted October 22, 1973.

• 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00. product was extracted with ether, the ether was evaporated, and the residue was vacuum-distilled. The isolated (I) had bp 58-58.5° (10 mm); n_D^{22} 1.4263; see [5].

CONCLUSIONS

To synthesize highly reactive anyl cyanates it is expedient to use cyanogen chloride as the acylating agent and run the synthesis with an equimolar ratio of the starting components.

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