INTER- AND INTRAMOLECULAR REARRANGEMENTS OF CYANURIC ACID TRIALLYL ESTERS

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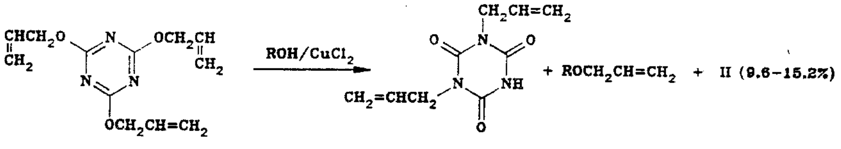
It is shown that the catalytic and thermal rearrangements of cyanuric acid triallyl esters to isocyanuric acid esters proceed via inter- and intramolecular mechanisms. Cross-reaction products are formed when the reaction is carried out with a mixture of homologs, while the reaction in the presence of a hydroxy-containing compound gives its allyl ether and diallyl isocyanurate.

The thermal rearrangement of triallyl cyanurate (I) to triallyl isocyanurate (II) is considered to be a special case of the Claisen rearrangement [1, 2]. The catalytic rearrangement of I is also known [3]. In addition, it has been shown that diallyl isocyanurate (III) and allyl alcohol are formed as the principal products in the reaction of triallyl cyanurate with water in the presence of cupric chloride as the catalyst [4].

The present research was devoted to a study of the reaction of cyanurate I with hydroxy-containing compounds and tri(methylallyl) cyanurate (IV) to ascertain the probable mechanism of the rearrangement.

Reactions of cyanurate I with allyl alcohol, acetic acid, and chloroacetic acid in the presence of cupric chloride in refluxing toluene at reagent molar ratios of 1:1, 1:2, and 1:3, respectively, were carried out. In all cases we obtained III and the corresponding allyl esters. The amount of isocyanurate II did not exceed 15%. This can be explained by assuming that intramolecular rearrangement of the allyl groups and an intermolecular reaction leading to replacement of the hydrogen atom in the proton-donor compounds by an allyl radical occur during the reaction.



I R=CH=CHCH$_2$, CH$_3$CO, ClCH$_2$CO III

It was established that the acidities of the hydroxy-containing compounds do not have a substantial effect on either the duration of the reaction or the ratio of products formed.

To confirm the expressed assumption regarding the occurrence of inter- and intramolecular reactions we carried out the corearrangement of I and IV, which were used in equimolar amounts. The process was carried out in solution in toluene by refluxing in the presence of a catalyst – cupric chloride. Absorption bands at 1700 and 770 cm^{-1}, which correspond to the >C=O group and constitute evidence that the formation of an isocyanurate structure occurred, are observed in the IR spectrum of the reaction products. It was established by mass spectrometry that four intense peaks with m/z 249, 263, 277, and 291 are present in the mass spectrum; two of these corresponded to the molecular ions of the products of intramolecular rearrangement, and the other two corresponded to the molecular ions of the products of a cross reaction, viz., to the molecular ions of isocyanurate II, diallyl methylallyl isocyanurate (V), allyl di(methylallyl) isocyanurate (VI), and tri(methylallyl) isocyanurate (VII).

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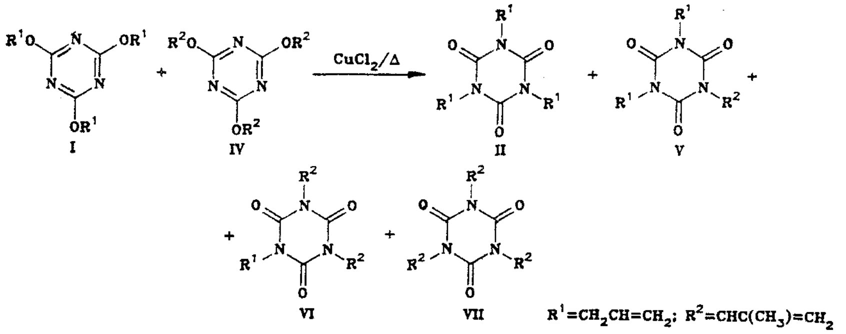
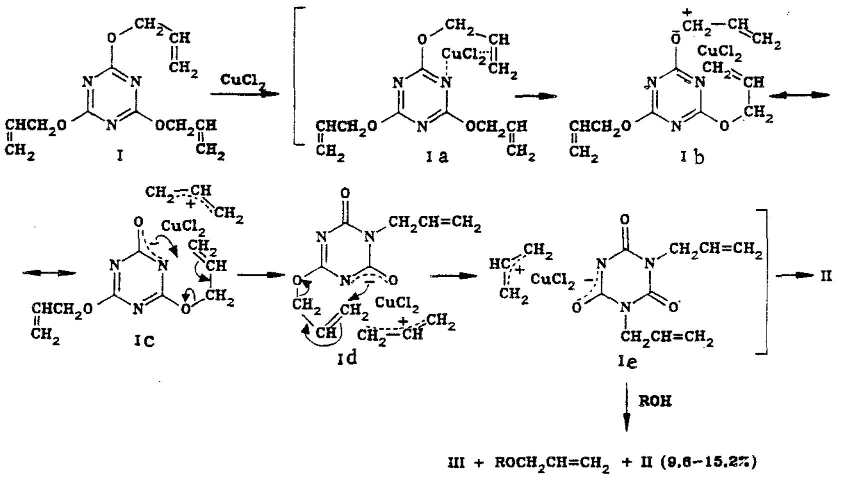
In the mass spectra of the products obtained by the thermal corearrangement of the above-named cyanurates we observed intense peaks of the same molecular ions as in the first case.



However, the ratios of the isocyanurates in these cases, which were found by chromatography [5], were different (see the experimental section). Thus, in the case of the catalytic rearrangement the mixture was enriched with cross-reaction products – V (40.4%) and VI (31.7%) – as compared with the calculated values. In addition, there is an increased overall amount of isocyanurates II and V (58.9%); in our opinion, this constitutes evidence for the higher reactivity of cyanurate I as compared with its substituted homolog. The latter can be explained by the steric hindrance caused by the methyl group, which hinders coordination with the bulky copper atom [6]. For example, the time required for rearrangement of cyanurate I with 1% of the catalyst is 10 min, while it increases to 4 h for cyanurate IV.

On the other hand, in the case of the thermal rearrangement the composition of the mixture obtained approaches the statistical composition.

From the information set forth above one can propose a scheme for the catalytic conversion of cyanuric acid allyl esters.



The formation of II proceeds through a step involving the coordination of cupric chloride with cyanurate I in intermediate Ia. It is known that sym-triazine derivatives are monodentate ligands with respect to the divalent copper ion; coordination takes place with an atom of the triazine ring [7]. It is also known that the allyl double bond is capable of complexing with transition metal ions [8]. In the case of cyanurate I coordination therefore occurs at both the nitrogen atom and at the allyl double bond (the same is true in the case of cyanurate IV). Compound Ia then undergoes heterolysis at the carbon–oxygen bond with the formation of ionic structure Ib, which undergoes intramolecular rearrangement, during which new intermediate complexes Id,e are formed successively. A new type of Claisen rearrangement, viz., anionic rearrangement, was previously observed in a study of enols of α-allyloxy ketones [9].

The reaction ends with catalytic rearrangement by reaction of anion Ie with the allyl (methylallyl) cation and the simultaneous liberation of the catalyst. The formation of an isocyanurate structure, which is energically more favorable than the cyanurate structure [10], promotes this transformation. When the rearrangement proceeds in the presence of hydroxy-containing compounds, in the final step of the reaction the allyl cation attacks this compound with subsequent transfer of a proton to the anion having an isocyanurate structure and the formation of isocyanurate III and the corresponding allyl esters.

The IR spectra recorded in the catalytic rearrangement of cyanurate I in toluene at 100°C with 0.5% of the catalyst do not contradict the proposed scheme. Thus, bands at 1540, 1730, and 800 cm^{-1}, which are absent in the spectrum of I, appear after 30 min. Bands at 1750, 1620, and 790 cm^{-1} are observed in the next 30 min. In conformity with the literature data [11], the band at 1540 cm^{-1} can be assigned to the conjugated $>C{=}N-$ group of intermediate complex Ib, the bands at 1730 and 800 cm^{-1} can be assigned to the $>C{=}O$ group of Id, and the bands at 1750, 790, and 1620 cm^{-1} can be assigned to the $>C{=}O$ and $>C{=}N-$ groups of Ie. The intensities of the bands that characterize the intermediate complexes increase with time up to certain maximum values, after which they decrease and disappear completely in an order that is the reverse of the order in which they appeared. The intensities of the bands at 1700 and 770 cm^{-1}, which are related to isocyanurate II, increase with time and reach their maximum values after 6 h [1].

EXPERIMENTAL

The mass spectra were recorded with an MI-1201 spectrometer with direct introduction of the samples into the source; the ionizing electron energy was 70 eV, and the temperature of the ionization chamber was 150°C. The IR spectra of solutions in toluene with a layer thickness of 0.05 mm were recorded with a UR-20 spectrometer.

Chromatography was carried out with a Tsvet chromatograph with a flame-ionization detector; the sorbent was 4% XE-60 on Chromosorb G, the temperature of the column was 140°C, and the carrier-gas (helium) flow rate was 33 ml/min.

Cyanurates I and IV were synthesized by the method in [12].

Diallyl Isocyanurate (III). A. A reactor equipped with a stirrer, a reflux condenser, and a thermometer was charged with 24.9 g (0.1 mole) of cyanurate I, 6 g (0.1 mole) of allyl alcohol, 0.75 g (3% of the mass of I) of $CuCl_2 \cdot 2H_2O$, and 40 ml of toluene, and the mixture was heated to the boiling point and refluxed for 2 h. It was then cooled, and the precipitate was removed by filtration, washed with a 2% solution of HCl, and dried to give 17 g (81.5%) of isocyanurate III with mp 145-146°C (mp 143-145°C [13]). The filtrate was washed with water (three 7-ml portions), dried over Na_2SO_4, and distilled at atmospheric pressure. According to the results of reaction with mercuric acetate [14], the distillate contained 0.08 mole (80%) of an unsaturated compound based on the diallyl ester. According to the results of GLC, 4.2 g of the still residue contained 3.8 g (15.2%) of isocyanurate II and 0.4 g (1.9%) of isocyanurate III.

B. The reaction was carried out as in method A, except that 6 g (0.1 mole) of acetic acid was used. The reaction gave 17.7 g (85%) of isocyanurate III with mp 145-146°C. Titration showed that the aqueous extract contained 0.01 mole (10%) of acetic acid; saponification showed that the distillate contained 0.083 mole (83%) of allyl acetate. IR spectrum: 1730 ($C{=}O$), 1640 cm^{-1} ($C{=}C$). The mass of the residue after removal of the solvent by distillation was 2.5 g, which consisted of 2.4 g (9.6%) of isocyanurate II and 0.1 g (0.5%) of isocyanurate III.

The reaction with chloroacetic acid was carried out similarly to give 19.2 g (91.5%) of isocyanurate III with mp 145-146°C. The aqueous extract contained 0.002 mole (2%) of unchanged acid. Vacuum distillation of the filtrate gave 11.1 g (82.5%) of allyl chloroacetate with bp 46-48°C (8 hPa) and n_D^{20} 1.4466 [bp 70-72°C (26.6 hPa) and n_D^{20} 1.4468 [15]]. According to GLC, the 3 g of still residue contained 2.6 g (10.5%) of isocyanurate II and 0.3 g (1.4%) of isocyanurate III, as well as a certain amount of allyl chloroacetate.

Corearrangement of Triallyl Cyanurate (I) and Tri(methylallyl) Cyanurate (IV). A. A reactor equipped with a reflux condenser and a thermometer was charged with 12.5 g (0.05 mole) of cyanurate I, 14.55 g (0.05 mole) of cyanurate IV, 0.27 g (2.16%) of $CuCl_2 \cdot 2H_2O$, and 45 ml of toluene, and the mixture was heated to the boiling point and refluxed for 4 h. It was then cooled and filtered. According to GLC, the mixture contained 18.5% isocyanurate II t_R = 11.0 min), 40.4% isocyanurate V (t_R = 11.5 min), 31.7% isocyanurate VI (t_R = 15.2 min), and 9.4% isocyanurate VII (t_R = 20.0 min).

B. A reactor was charged with 12.5 g (0.05 mole) of isocyanurate I and 14.55 g (0.05 mole) of isocyanurate IV, and the mixture was heated to 190-200°C and maintained at that temperature for 5 h. It was then cooled, and the resulting partially polymerized mass was pulverized and extracted with toluene. According to GLC, the toluene extract contained 23.3% isocyanurate II, 24.0% isocyanurate V, 31.6% isocyanurate VI, and 21.1% isocyanurate VII.

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TRANSFORMATION OF DIHYDRO-1,5-BENZODIAZEPIN-2-ONES UNDER THE INFLUENCE OF ACETIC ANHYDRIDE

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The acylation of 4-R-2,3-dihydro-1H-1,5-benzodiazepin-2-ones leads to isomerization or opening of the heteroring with subsequent acylation. 1-Acyl-2,3-dihydro-1,5-benzodiazepin-2-ones are not formed.

We have previously synthesized 1,5-diacyl-2,3,4,5-tetrahydro-1H-1,5-benzodiazepin-2-ones, which are of interest from both chemical and biological points of view [1]. Continuing our research in this area we have studied the reaction of 4-methyl- and 4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (I, II) [2, 3] with acetylating agents.

The reaction of I with a 4.5-fold excess of acetic anhydride in toluene by the method in [1] led only to pronounced resinification. At the same time, carrying out the reaction in chloroform gave a mixture of substances, the principal component of which was acetoacetic acid N-(2-acetamidophenyl)-amide (III).

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