ON THE TWO-STEP SYNTHESIS OF AROYLENEBENZIMIDAZOLES

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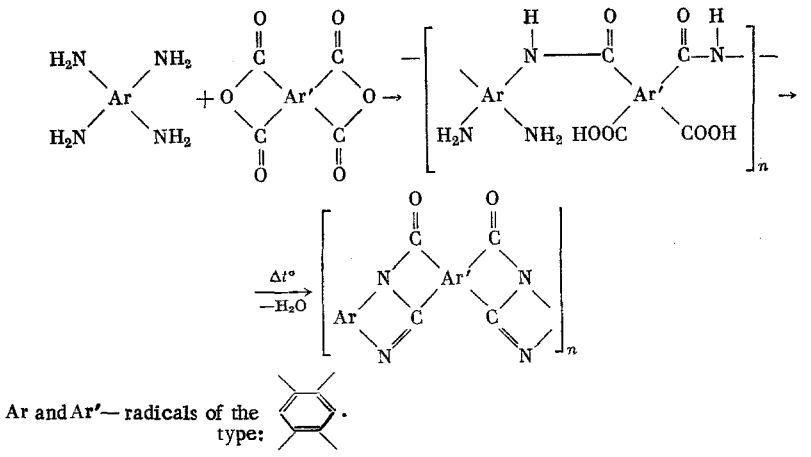
In recent years the synthesis of ladder polymers has attracted attention; these molecules are constructed from two cross-linked chains. These polymers should have increased stability to various degrading forces, such as thermal degradation [1-7]. Conspicuous among ladder polymers are those containing heterocycles, notably the pyrrone polymers [8, 9], which are usually prepared by the two-step reaction of aromatic tetracarboxylic acid dianhydrides with aromatic tetraamines

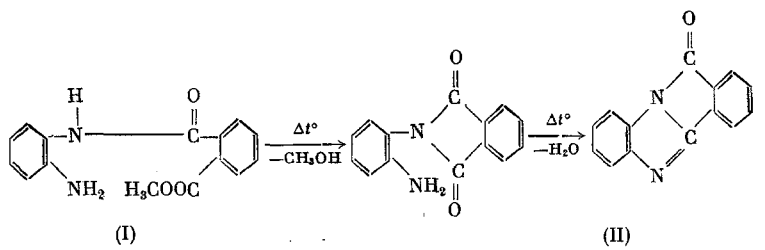


Ar and Ar′— radicals of the type: .

This scheme does not fully represent the actual reaction sequence of the thermal cyclization of polyamide amino acids (PAAA), because of the factors specifically associated with the process of solid-state cyclization and originating from the limited mobility of the polymer chains. As a result, the polymer contains incompletely cyclized segments, incorporating amide amino acid, imide amine, and carboxybenzimidazole units. Moreover, cyclization is accompanied by side reactions, such as decarboxylation of the PAAA [10]. The presence of anomalous units in the polymer chains considerably reduces the thermal stability of polyaroylenebenzimidazoles [10-13].

Use of 2,5-bis(methoxycarbonyl)terephthaloyl chloride as starting compound might well prevent decarboxylation and promote a higher degree of cyclization. In this context we decided to study the preparation of aroylenebenzimidazoles as exemplified by the cyclization of the hitherto undescribed model compounds 2-methoxycarbonyl-N-(o-aminophenyl)benzamide (I) and 2,5-bis(methoxycarbonyl)-N,N'-bis(o-aminophenyl)-terephthalamide (III).

Analogy with PAAA [14, 15] suggests that the formation of aroylenebenzimidazoles based on polyamide amino esters will proceed in two steps: imidization and formation of the benzoylenebenzimidazole structure



(I) (II)

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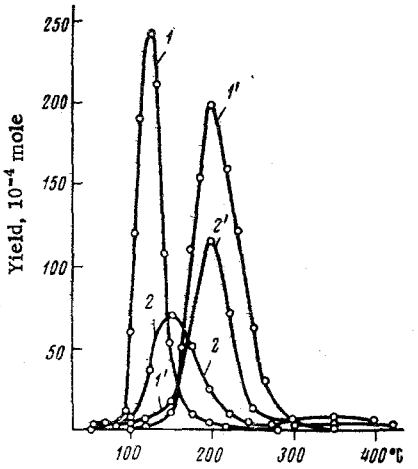


Fig. 1

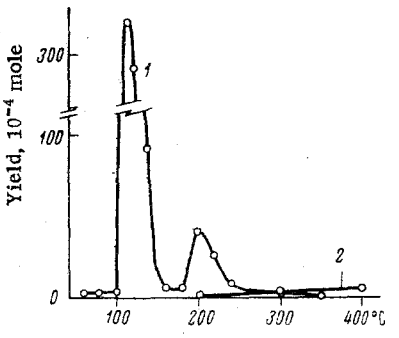
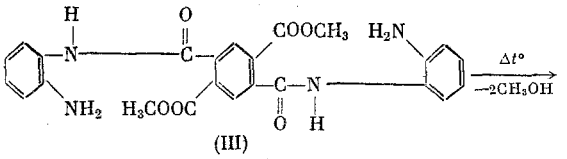


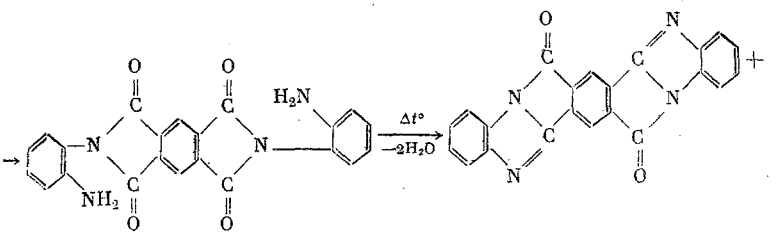
Fig. 2

Fig. 1. Temperature dependence of the yield of volatile products from the thermal cyclization of compounds 1, 2) I and 1', 2') III: 1, 1') methanol; 2, 2') water.

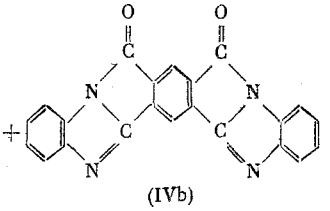
Fig. 2. Temperature dependence of the yield of volatile products from the thermal cyclodehydration of compound (V); 1) water; 2) CO_2.



(III)



(IVa)



(IVb)

We made a comparative GLC analysis of the volatile products of the thermal cyclization of N-(o-aminophenyl)phthalamic acid (V) and the model compounds (I) and (III). The volatile reaction products from (I) and (III) are methanol and water (Fig. 1), while compound (V) forms water and CO_2 (Fig. 2), which result from thermal decarboxylation under the conditions of cyclodehydration. Consequently it is extremely difficult to deduce the sequence of cyclization reactions involved in the preparation of aroylenebenzimidazoles from amide amino acids and the ratio of the rates of these reactions over a wide temperature range, since the sole reaction product from cyclization of (V) is water (Fig. 2).

The formation of aroylenebenzimidazoles involves two steps (Fig. 1); rapid liberation of methanol takes place first at lower temperatures, due to imidization. After compounds (I) and (III) have been heated under vacuum at 160°C for 1 h, the IR spectra of their cyclization products show absorption bands characteristic of the imide ring (1780, 1720, 1380, 730 cm^{-1} [16, 17]) and lack bands characteristic of the ester group (1735 and 1165 cm^{-1}) and of the amide group (1500 [16], 1640, and 3200 cm^{-1} [17]). The second step, formation of the benzoylenebenzimidazole ring, is slower than imidization, as can be deduced from the liberation of water.

This thermal intramolecular elimination is a true solid-state reaction, since (Fig. 1) cyclization of compounds (I) and (III) takes place at temperatures below their melting points [the mp of (I) is 145°C; that of (III) is >300°C].

The thermal conversions of model compounds (I) and (III) to (II) and (IVa, b) are accompanied by the disappearance of the absorption bands of the starting compound, 1165 cm^{-1} (C—O, methyl ester of carboxylic acid) [18], 1735 cm^{-1} (C=O, ester group) [18], 2960 cm^{-1} (CH_3) [18], 1500, 3200, and 1640 cm^{-1} (NHCO) [16, 17], 1600 and 3400 cm^{-1} (NH_2) [17, 16], and by the appearance of bands characteristic of benzoylenebenzimidazoles, 1450 and 1620 cm^{-1} (C=N) and 1760 cm^{-1} (C=O) [16, 17].

EXPERIMENTAL

Thermal cyclization was carried out in a quartz microreactor [19] under argon between 65 and 400°C; subsequent analyses used an LKhM-8MD chromatograph (model 5) [detection by katharometer; linear temperature programing, 12 deg/min, 35 to 160°C; argon flow rate 40 ml/min; 220 × 0.3 cm stainless-steel column, Porapak R (100-120 mesh)]. The heating time at each temperature was 10 min; the sample weight, 10 mg. The IR spectra were recorded with a UR-20 spectrometer (KBr disks).

2-Methoxycarbonyl-N-(o-aminophenyl)benzamide (I). To a stirred solution of o-phenylenediamine (2.44 g, 0.026 mole) [purified by two vacuum sublimations (0.5 mm, 80°C)] in dry CH_2Cl_2 (130 ml) in a stream of argon was gradually added o-(methoxycarbonyl)benzoyl chloride (2.25 g, 0.0113 mole). After 2.5 h stirring the precipitated o-phenylenediamine hydrochloride was filtered off. The mother liquor was cooled and mixed with ether. The resulting precipitate was filtered off, washed with ether, and dried in air and then under vacuum. The yield of (I) was 2.1 g (63.6%), as a pink powder with mp 149-150°C. Found: C 66.32; H 5.17; N 10.11%. $C_{15}H_{14}N_2O_3$. Calculated: C 66.6; H 5.18; N 10.38%. IR spectrum (ν, cm^{-1}): 1735 (C=O, aromatic acid ester), 1165 (C—O, methyl ester of carboxylic acid), 2960 (CH_3) [18], 3400 (NH_2), 1640, 1500 (NHCO) [16]. The content of NH_2 groups was 5.85% (calculated 5.90%), derived by the photocolorimetric method of [20].

1,2-Benzoylenebenzimidazole (II). Cyclization of I) at 300°C under vacuum gave (II) as yellow crystals with mp 212°C [16].

2,5-Bis(methoxycarbonyl)-N,N'-bis(o-aminophenyl)terephthalamide (III). To a stirred solution of o-phenylenediamine (0.432 g, 0.004 mole) in absolute $CHCl_3$ (10 ml) in a stream of argon was gradually added a solution of 2,5-bis(methoxycarbonyl)terephthaloyl chloride (0.638 g, 0.002 mole) (prepared by the procedure of [21]) in $CHCl_3$ (120 ml). After 6-h stirring the precipitated (III) was filtered off, washed with $CHCl_3$, and dried under vacuum over paraffin at 60°C. The dry product (III) was washed with soda solution to pH 7, and then with water and ethanol, and dried under vacuum at 100°C over P_2O_5. The yield of (III) was 0.894 g (95.3%), as yellow powder with mp >300°C (decomposition). Found: C 62.64; H 4.66; N 12.10%. $C_{24}H_{22}N_4O_6$. Calculated: C 62.40; H 4.77; N 12.15%. IR spectrum (ν, cm^{-1}): 1600 (NH_2), 3200, 1640 (NHCO) [17], 1735 (C=O, ester group), 1165 (C—O, methyl ester of carboxylic acid), 2960 (CH_3) [18]. The content of NH_2 groups was 6.76% (calculated 6.80%), derived by the photocolorimetric method of [20].

Mixed Isomers 7H, 15H-Bisbenzimidazo[1,2-*a*:1',2'-*a*']benzo[1,2-c:4,5-c']dipyrrole-7,15-dione (IVa) and 13H, 15H-Bisbenzimidazo[1,2-*a*:1',2'-*a*']benzo[1,2-c:4,5'-c'] dipyrrole-13,15-dione (IVb). Cyclodehydration of (III) at 200°C under vacuum gave (IVa, b) as an orange powder with mp >400°C. Found: C 72.85; H 2.80; N 15.38%. $C_{22}H_{10}N_4O_2$. Calculated: C 72.92; H 2.72; N 15.46%. IR spectrum (ν, cm^{-1}): 1760 (C=O), 1620 (C=N), 720 (C=O), which is consistent with the IR spectra of isomers (IVa) and (IVb) prepared by another method [17]. Absorption bands of (III) were absent, (ν, cm^{-1}): 1600 (NH_2), 1640, 3200 (NHCO) [17], 1735 (C=O, ester), 1165 (C—O, methyl ester of carboxylic acid), 2960 (CH_3) [18].

CONCLUSIONS

1. We have used thermal cyclization to synthesize aroylenebenzimidazoles based on the hitherto unknown amide amino esters 2-methoxycarbonyl-N-(o-aminophenyl)benzamide and 2,5-bis(methoxycarbonyl)-N, N'-bis (o-aminophenyl)terephthalamide.

2. We have used GLC to examine the liberation of the volatile products from the thermal cyclization of 2-methoxycarbonyl-N-(o-aminophenyl)benzamide and 2,5-bis(methoxycarbonyl)-N,N'-bis(o-aminophenyl)terephthalamide and have demonstrated the two-step nature of the formation of aroylenebenzimidazoles.

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REACTIONS OF β,β-DICHLOROVINYL ORGANYL SULFIDES WITH THIOLS AND THE SYNTHESIS OF BIS(ORGANYLTHIO)ACETYLENES

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β,β-Dichlorovinyl ethers, $Cl_2C=CHOR$, and the analogous sulfides, $Cl_2C=CHSR$, react in the same way with electrophiles and are distinguished from the corresponding unsubstituted vinyl compounds by their lower reactivity [1-4]. However, they differ markedly in their response to nucleophiles: the oxygen analogs are inert [2], while β,β-dichlorovinyl sulfides are readily dehydrochlorinated, forming α-chloro-β-(alkylthio)acetylenes [5], and undergo substitution of one of the chlorines with metal thiolates [6].

Our intention here was to examine the reaction of β,β-dichlorovinyl sulfides with thiols in the presence of alkali, which we thought relevent to the preparation of various unsaturated sulfides and as a new model for nucleophilic substitution at an unsaturated carbon atom. We found that the reaction can follow several pathways, depending on the conditions

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