THERMAL REACTIONS OF 1-ARYL-5-METHYLTETRAZOLES

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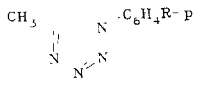
The mechanism of the thermal reactions of 1-aryl-5-methyltetrazoles, which involve isomerization to the azide, elimination of a nitrogen molecule, and the formation of singlet nitrenes followed by isomerization to benzimidazoles and carbodiimides, has been studied by combining the methods of derivatography and the current arsenal of mass-spectrometric techniques. The influence of the electronic properties of the substituent (in the para position of the benzene ring) on the course of the thermolysis has been established.

We previously showed [1] that the thermolysis of 1-phenyl-5-methyltetrazole takes place with the formation of aniline, 2-methylbenzimidazole, sym- and asym-methylphenylcarbodiimides, and their polymerization products, as well as guanidines. For the purpose of precisely determining the thermolysis mechanism, which determines the particular composition of the products, in the present work we studied the thermal conversions of a new group of substituted 1-aryl-5-methyltetrazoles (I-III).



I-III

I $R=CH_3$; II $R=NO_2$; III $R=NH_2$

The problem posed was solved on the basis of a set of derivatographic and mass-spectrometric methods, which were employed in the following sequence:

1. Derivatographic analysis of original compounds I-III (Fig. 1), whose results were used to determine the exact values of the temperatures of the phase and chemical conversions. The melting of tetrazoles I-III was reflected by an endothermic effect on the DTA curve with a maximum at 120, 145, and 150°C, respectively (Fig. 1). The nature of the thermal effects was determined on the basis of the derivatogram, and the kinetics of the evolution of the gases during the thermal reactions (the high-temperature processes with the evolution of heat and a loss of weight) were studied.

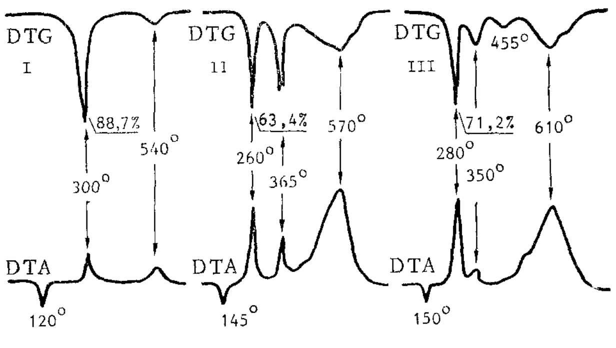


Fig. 1. Differential thermal analysis (DTA) and derivative thermogravimetry (DTG) or 1-aryl-5-methyltetrazoles I-III.

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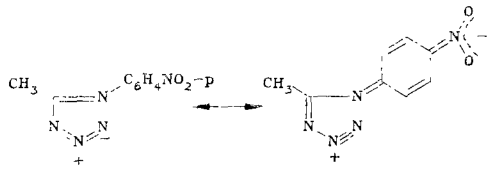
2. Thermolysis of tetrazoles I-III, which was carried out with exact observance of the conditions of the derivatographic analysis (see Experimental) with heating of the sample directly in the crucible of the derivatograph and or in a sealed glass ampul.

3. Mass-spectrometric identification of the thermolysis products and an analysis of the qualitative and quantitative changes in the composition of the pyrolysate with the collection of samples at various temperatures in the vicinity of the maxima of the thermal reactions (Fig. 1).

This sequence of experimental methods not only provides the information enumerated, but also has the advantage that it makes it possible to trace the dynamics of the shaping of the composition of the products as the temperature is increased and to thereby establish the sequence of formation and the nature of the further chemical conversions of the individual components of a pyrolytic mixture. The results of the present work, which were obtained according to the experimental plan just described, provdies some basis to treate the thermolysis of 1-aryl-5-methyltetrazoles I-III as a set of parallel and consecutive reactions, whose initial step is isomerization of the orginal compounds to the azide tautomeric form.

The formation of an azide structure during the heating of 1,5-disubstituted tetrazoles was previously postulated in [2, 3]; however, this opinion is not shared by all investigators (see, for example [4, 5]). In our case, isomerization in the initial stages of thermolysis is indicated by the following findings: 1) the presence of an endothermic effect preceding the chemical reaction with the evolution of heat on the DTA curve of tetrazole I (Fig. 1; as expected, this feature is displayed by the compound most stable with respect to heating); the endothermic nature of the tautomeric conversions in a number of 1,5-disubstituted tetrazoles was previously noted in [6, 7]; 2) the minimal temperature for the decomposition of tetrazole II (Fig. 1), which is due to the stabilization of the azide structure by the presence of the electron-acceptor substitutent, i.e., the nitro group;



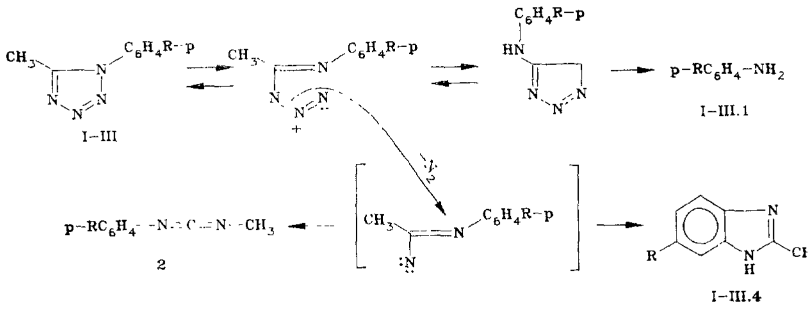
3) the first order of the loss of weight for the decomposition of 1-phenyl-5-methyltetrazole [1], which does not contradict the kinetic scheme

$$\text{tetrazole} \rightleftarrows \text{azide} \rightarrow \text{reaction products;}$$

4) the composition of the thermolysis products (Table 1), which has much in common with the known thermal reactions of organic azides [8, 9]. The high-temperature reactions with a weight-loss maximum and an exothermic effect at 540 (for I), 365 and 570 (for II), and 350 and 610° (for III) are caused by the decomposition of the compounds indicated in Table 1 and will not be discussed in this communication.

In this context we should mention the 2-substituted 2-methyl-benzimidazoles (4) and N-methyl-N'-arylcarbodiimides (2 and 2a), whose accumulation in the pyrolytic mixture takes place simultaneously with the decomposition of the original tetrazoles I-III. The configuration of these compounds corresponds to the structure and reactivity of the intermediate nitrene formed upon the thermolysis of the azide with the elimination of molecular nitrogen (see the reaction scheme). The fact that products of bimolecular reactions of the nitrene (recombination, addition at the double bond, the formation of primary amines) are not detected during the analysis of the pyrolysate conforms to the ideas concerning the singlet spin state of the biradicals associated with the thermal decomposition of azides [11-13], as well as the low (in comparison to an intramolecular rearrangement) rate of the singlet–triplet transition at high temperatures characteristic of the present experiment [14, 15].

Another finding attesting to the intermediate formation of nitrenes is the variation of the relative content of benzimidazoles as a function of the electronic properties of the substituent R (Table 1). In accordance with the expected distribution of the electron density of the aryl fragment of compound II, the total yield of benzimidazoles in this case is higher than in the case of the thermolysis of other tetrazoles.



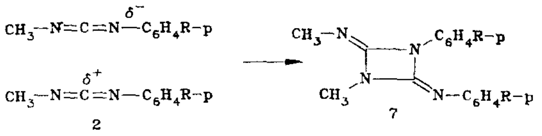
The thermolysis products directly associated with the decomposition of the original tetrazoles also include anilines (1) (Table 1). The proposed mechanism for this reaction is hypothetical to a great extent. However, such rearrangements with the intermediate formation of an azide tautomer are well known among 5-substituted amino- and mercaptotetrazoles [6, 16].

The thermolysis of tetrazoles I-III is not restricted only to the formation of the benzimidazoles (4), carbodiimides (2), and anilines (1) considered. An appreciable role in the shaping of the composition of the products is occupied by secondary processes, among which the leading spot belongs to the polymerization of the asym-carbodidmides.

The reactivity of the heterocumulenes in these processes is determined by the structure of the substituent R. This is reflected in the relative content of the free carbodiimide and the polymerization products. For example, the free carbodiimide is not observed among the components of the pyrolysate of compound II. On the other hand, in the case of compound III, its content is especially high, while polymers are not detected (Table 1).

Another special feature of the reactions under consideration in the dimerization step is the formation of only one of the six possible isomers with consideration of the inequivalence of the $C{=}N$ bonds and the possibility of addition of the "head-to-tail" and "head-to-head" types (Table 1) [1]. Similar specificity was also noted in the reactions of ketenes with carbodiimide [17] and sulfodiimide [18]. In analogy to the mechanism of these reactions [19], the dimerization of the asym-carbodiimides (2) in our case may be represented by a scheme of dipolar 1,2-cycloaddition.

In the conjugated carbodiimide structure the tendency for separation of charges is enhanced by the inductive effect and is weakened by the mesomeric effect of the nitro and amino groups, respectively. As a consequence, in the pyrolysates of II and III there is a sharp difference between the content of the free carbodiimide and its dimer, as well as the higher polymerization products (see Table 1).

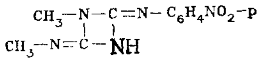
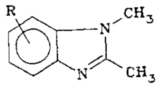
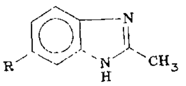
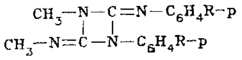
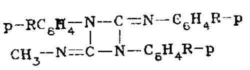
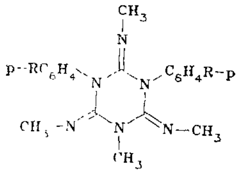
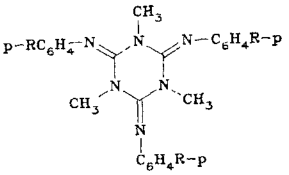


The formation of asym-carbodiimide trimers I-II.12 is not unequivocal as the dimerization process. For example, two isomeric products were found in the pyrolysate of 1-phenyl-5-methyltetrazole [1] (the structural formula of one of the isomers is given in Table 1).

As the temperature is increased, the polymerization products considered decompose into N,N'-diaryl- (I, II.6) and N,N'-dimethylcarbodiimides [the intermediate formation of the latter is evinced by the presence of the corresponding quanidines (I, II.5) and polymers (I, II.11) among the products]. Evidence of the origin of the sym-cumulenes is provided by the fact that they were discovered in the pyrolysate only in the case of the tetrazoles whose thermolysis is accompanied by the polymerization of N-methyl-N'-arylcarbodiimides (Table 1). A similar pattern was previously noted for the thermal and photochemical decomposition reactions of the phenyl isocyanate dimer, which take place with the formation of CO_2 and N,N'-diphenylcarbodiimide [20].

The subsequent conversions of the sym- and asym-carbodiimides were represented either by copolymerization (the products of this reaction are compounds I.10, I.11, II.10 and II.11) or the formation of quanidines (I, II.5, 8, 9) when they are reacted with anilines.

TABLE 1. Thermolysis Products of 1-Aryl-5-methyltetrazoles I-III*

Compound	Structure	Yield, %		
		I	II	III
1	p-R—C_6H_4—NH_2	2,2	9,5	3,5
1a	p-O_2N—C_6H_4—$NHCH_3$	—	11,0	—
1b		—	7,0	—
1c	p-O_2N—C_6H_4—N—C_6H_4—NO_2-p	—	21,0	—
1d	$(CH_3)_2C{=}N$—C_6H_4—NH_2-p	—	—	1,8
1e	$(CH_3)_2C{=}N$—C_6H_4—$N{=}C(CH_3)_2$-p	—	—	2,2
2	CH_3—$N{=}C{=}N$—C_6H_4—R-p	7,3	—	—
2a	$(CH_3)_2C{=}N$—C_6H_4—$N{=}C{=}N$—CH_3-p	—	—	90,0
3		2,7	16,0 18,0	—
4		48,7	17,0	2,5
5	CH_3—NH—$C(=NCH_3)NH$—C_6H_4—R-p	5,5	+†	—
6	p-R—C_6H_4—$N{=}C{=}N$—C_6H_4—R-p	19,0	+	—
7		5,8	+	—
8	p-CH_3—NH—$C(=N$—C_6H_4—$R)NH$—C_6H_4—R-p	4,3	+	—
9	p-R—C_6H_4—NH—$C(=NC_6H_4$—$R)NH$—C_6H_4—R-p	4,5	+	—
10		+	+	—
11		+	+	—
12		+	+	—

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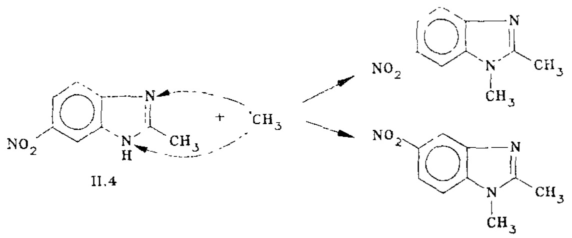
*The relative yield of the thermolysis products correspond to the maximum temperature of the first weight-loss peak and the exothermic effect (see Fig. 1).

† The pyrolysate components not separated by GLC are indicated by a plus sign; the evidence supporting the structures of these compounds were given in [10] (see also the experimental part of that work).

The thermolysis products of tetrazole III include compounds which originate as a result of the reaction of individual components of the pyrolysate with acetone, which served as the solvent for the GLC separation.

In conclusion, we mention a number of processes which take place with the participation of radicals. The general reaction of this type is the formation of 1,2-dimethylbenzimidazoles (I, II.3, Table 1). In the pyrolysate of nitro derivative II, this compound was represented by two isomers, whose origin is illustrated by the following scheme:



II.4

II.3

Another example of radical reactions is the formation of N-methyl-p-nitroaniline (II.1a) and 4,4'-iminonitrobenzene (II.1c). The sources of the radicals in this case are the decomposition reactions of the polymerization products of the carbodiimides, as is confirmed by the structure of 1,3-diazetidine (II.1b, Table 1).

In the composition of pyrolysates I-III we identified (see Experimental) compounds comprising 93.3% of the total quantity of the components of the pyrolytic mixture, whose total yield amounted to 97.0%.

EXPERIMENTAL

The method of synthesis and the physicochemical characteristics of the 1-aryl-5-methyltetrazoles investigated (I-III) were presented in [21].

The DTA and DTG data (Fig. 1) were obtained on a MOM OD-102 derivatograph (Hungary) under the following conditions: a nitrogen atmosphere; temperature range, 20-800°C ($V = 5°C/min$); sample weight, 100 mg; reference, Al_2O_3.

The analysis of the qualitative and quantitative composition of the pyrolysate samples was carried out on a Varian MAT-311A mass spectrometer with the use of the methods of low- and high-resolution mass spectrometry ($\Delta M/M = 15,000$, PPA as a reference), mass fragmentography, the field-desorption technique, and gas-chromatographic—mass spectrometry. The conditions for recording the mass spectra were standard and were described in [1, 10]. The identification of the components in the pyrolysates was based on the agreement between the times of emergence (t_{min}) from the column, the chromatographic mobility (R_f), and the mass spectra for the reference substances.

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