Journal of Thermal Analysis, Vol. 32 (1987) 1957–1967

SUBSTITUTED 2,5-DIARYL-2H-TETRAZOLES

A combined investigation of their thermal behaviour by simultaneous thermal analysis, mass spectrometry and high-performance liquid chromatography

M. Feist, Ch. Csongár and *L. Adler*

SEKTION CHEMIE DER HUMBOLDT-UNIVERSITÄT ZU BERLIN, HESSISCHE STR. 1,
BERLIN, 1040, GDR

(Received February 6, 1987)

Elimination of nitrogen from diaryl substituted 2H-tetrazoles during the first step of thermal decomposition yields diphenylnitrileimines. In spite of the drastic reaction conditions of the melt, they react relatively selective, giving two main products, the 1,2,4,5-tetrazines and 1,2,4-triazoles (together more than 70%). The triazoles are formed if the separation of nitrenes from the nitrileimine is favoured. Therefore, the mass losses found for the first step exceed the values calculated for N_2 only. The product mixture after the first TG step was investigated by the title methods, and especially by means of computer-aided MS analysis.

The well-known elimination of molecular nitrogen from 2H-tetrazoles [1] can be initiated by photochemical or thermal activation in dilute solutions [2, 3], as well as in PMMA matrices, e.g. as used for photo resist systems [4]. We investigated the thermal behaviour of the pure diaryl-substituted 2H-tetrazoles for a comparison with the behaviour in dilute solutions, further assuming that the decomposition mechanism should be simple and well analysable by thermogravimetry (TG). However, it was found that the first step of decomposition from the melt could not be explained simply by the elimination of nitrogen and subsequent dimerization of the nitrileimines formed in the initial step. The found mass losses considerably exceeded the values calculated for 1 N_2 [5], showing that the stabilization of nitrileimines is a more complicated process. In order to clarify the behaviour in the reaction, the products existing after the first TG step were investigated through mass spectrometry (MS), high-performance liquid chromatography (HPLC) and UV spectroscopy.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Results and discussion

Thermoanalytical curves (T, DTA, TG, DTG)

The title compounds were investigated up to 480° at linear heating rates in a dried inert gas flow (Table 1). The characteristic shape of the thermoanalytical curves is determined by a sharp melting peak, followed by a strong exothermic reaction peak (Fig. 1a). The exothermic DTA peak is accompanied by a mass loss Δm_1, mostly well separated from the further mass losses Δm_2 and Δm_3 (Fig. 1b). Whereas the first TG step is evaluable quantitatively, the further mass loss between 220 and 460° is unspecific. Δm_2 and Δm_3 are almost endothermic, with very weak and broadened DTA effects (T_p from 285 to 340°), but a region of nearly constant mass is attained up to 460°.

For the compounds *1b, 1c, 1k, 2a, 2c, 2g* and *2k*, one can separate only one further TG step, Δm_2, and the decomposition does not attain a plateau up to 460°. Therefore, these substances have structureless DTA curves after the exothermic peak, without indication of endo- or exothermal decomposition. Only the hydroxy compound *2c* seems to decompose exothermically in the upper temperature region.

According to the width of the temperature interval between the melt and the beginning of mass loss, one can distinguish three types of DTA curves: (1) The

Table 1 Results of thermogravimetric and enthalpimetric analysis

N°	X	Y	E, mg	Δm_1, %	Δm_2, %	Δm_3, %	n_{N_2} (Δm_1), mol	$-\Delta H$ (Δm_1), J mol^{-1}
1a	H	NMe_2	4.38	32.65	56.62		3.9	167
1b	H	NH_2	5.03	32.60			1.4	173
1c	H	OH	5.06	32.30			2.7	196
1d	H	OMe	2.78	23.74	47.33	11.33	2.1	135
1e	H	Me	4.52	34.52	46.90		2.9	152
1f	H	H	3.19	32.29	57.05		2.6	139
1g	H	F	2.99	27.10	38.63	11.84	2.3	144
1h	H	Cl	7.29	19.75	60.90		1.8	164
1j	H	Br	5.16	16.67	44.96	14.53	1.8	176
1k	H	CN	3.05	11.15	9.51		1.0	162
1l	H	NO_2	3.34	14.07	52.99		1.3	69
2a	NMe_2	H	2.91	15.12	65.98		1.8	135
2c	OH	H	2.87	14.63	27.87		1.2	126
2d	OMe	H	2.59	18.53	56.37		1.7	118
2g	F	H	5.61	28.34			2.4	135
2j	Br	H	2.95	17.97	62.37		1.9	141
2k	CN	H	4.84	17.98			1.6	142
2l	NO_2	H	7.07	16.25	9.38	30.31	1.6	65

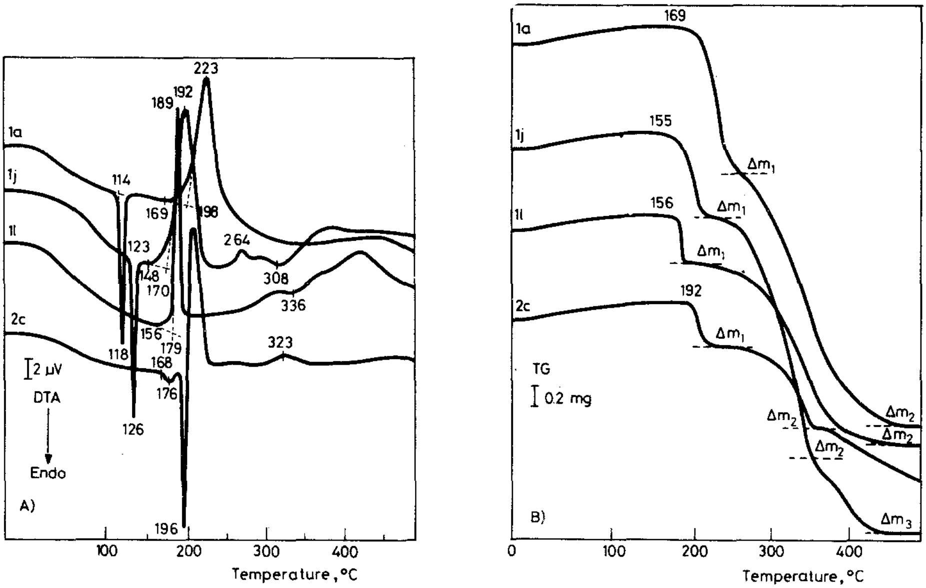


Fig. 1a, b Typical DTA and TG traces. Heating rate: 5 deg/min, 70 ml N_2/min

substances *1c, 1k, 2c* and *2l* decompose during melting; therefore, only the flank side of the melting peak can be recorded and very sharp exothermic peaks follow. (2) Most of the compounds give stable melts (e.g. *1a* and *1j* in Fig. 1a), and after different temperature intervals (up to 60° for *1d*) decomposition starts, giving broad, shoulder-free reaction peaks. (3) The nitro compound *1l* decomposes explosively without melting, which is in accordance with literature data on other nitroaryl-substituted tetrazoles [6] (Fig. 1a, b).

Two compounds show an endothermic effect before melting (*1b*: $T_{\text{on}}^{\text{ex}}$ 146°, T_p 150°; *2c*: $T_{\text{on}}^{\text{ex}}$ 168°, T_p 176°), which has been attributed to a phase transition not further investigated.

Figure 2 demonstrates the shifts of the DTA peak maxima of the exothermic reaction peak depending on the 2-aryl substituent [5]. A considerable influence of the substituent was found for the 2-aryl-5-phenyl-2H-tetrazoles, whereas the 5-aryl-2-phenyl-2H-tetrazoles do not show a remarkable variation; rather a contrary dependence can be seen. Such a contrary course of decomposition temperatures in the case of C- or N-side substitution has also been reported for some stilbenyl-substituted 2H-tetrazoles [7].

Moreover, it was investigated whether the exothermicity of the first decomposition step is influenced by various substituents. For this, an average heat transfer constant of the sample holder was estimated for the temperature region of

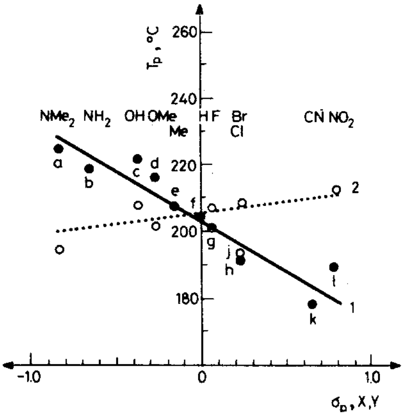


Fig. 2 Shift of the DTA maxima of the first exothermic decomposition step depending on the aryl substituent. *1:* 2-aryl-5-phenyl-2H-tetrazoles, *2:* 5-aryl-2-phenyl-2H-tetrazoles (see Table 1)

interest (170–220°), using the literature recommendations [8]. The enthalpy values were estimated with $K = 360$ mJ deg^{-1} min^{-1} and the graphically found peak areas. The values listed in Table 1 do not exhibit any dependences. They represent orientational values only, because the process investigated is obviously a complex one. It is further known that enthalpimetry by DTA provides rather inaccurate data.

Analysis of the product mixtures after the first TG step

Sample preparation

The temperatures at which the first TG step ended (T_{MS} in Table 3) were taken from the TG traces of compounds with well-separated Δm_1. In a second run, the samples were heated up to these temperatures and then quenched to room temperature (15 s). The brown product mixture was completely dissolved in methylene chloride and then analysed. Only the two hydroxy compounds *1c* and *2c* yielded coaled products insoluble in CH_2Cl_2 after the first TG step, and these were therefore not analysed further.

In order to prove that mass changes or transitions do not occur during cooling, cooling curves of the product mixtures from *1f* and *1h* were recorded ($T_{max} = T_p + 10$). Neither mass changes nor DTA effects were recognized.

Analysis

Analysis by means of HPLC and MS of the product mixture obtained after the first TG step of *1f* led to the coincident results that only two main products were formed (more than 70% of the total mixture). In spite of the drastic conditions in

Table 2 Identification of the main products separated chromatographically

Educt	X	Y	Products	M.p., °C	λ_a^{max}, nm	$M\urcorner^{+}$, (rel. intens.)
1f	H	H	*3f*	204 [10] 205	332	388 (47%)
			4f	106 [1] 103	246	297 (33%)
1h	H	Cl	*6h*		333	456 (50%)
			5h		247	331 (12%)
2g	F	H	*3g*	89–90	330	424 (24%)
			4g	128–31	244	333 (25%)

the melt, the nitrileimines formed during nitrogen elimination obviously react selectively.

In the case of the unsubstituted diphenyl compound *1f*, the postulated main products (Fig. 3) were available in substance, thereby permitting identification by HPLC as well as estimation of the mass ratio of the products. The chromatogram obtained is shown in Fig. 4. *1f* is not detectable in the mixture. The ratio of the two main products, 1,3,5-triphenyl-1,2,4-triazole *(5f)* and 1,3,4,5-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine *(3f)*, is 2.2 : 1.

Identical results were obtained for the other product mixtures. In these cases, the respectively substituted triazoles and tetrazines were missing and could not be used as authentic substances for comparison. Thus, the sequence of retention times found for *1f* (1,2,4-triazole < tetrazole < tetrazine < 1,2,3-triazole) was assumed to

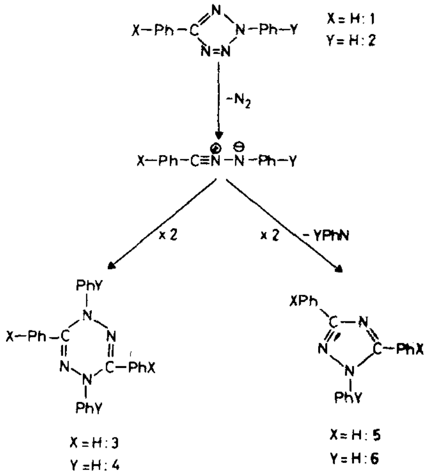


Fig. 3 Formation of tetrazines (*3; 4*) and triazoles (*5; 6*) from nitrileimines

Table 3 Mass spectra of the main products after the first TG step Δm_1 (calculated with SEKOS)

Tetrazole (*1*; *2*)				Tetrazine (*3*; *4*)							Triazole (*5*; *6*)					
N°	X	Y	T_{MS}[1]	t_{max}[2]	%TIC[3]	$M^{\rceil +}$(%)	*a* (%)	*b*	*c*	*d*	t_{max}[2]	%TIC[3]	$M^{\rceil +}$(%)	*e*	*b*	*c*
1d	H	OMe	236	5.4	33	448 (76)	210 (100)	121 (43)	103 (5)	107 (19)	3.9	42	327 (16)	224 (4)	121 (100)	103 (8)
1f	H	H	230	7.3	28	388 (45)	180 (59)	91 (23)	103 (5)	77 (100)	5.9	48	297 (21)	194 (34)	91 (100)	103 (9)
1h	H	Cl	224	5.2	27	456 (50)	214 (67)	125 (26)	103 (9)	111 (100)	3.9	46	331 (12)	228 (14)	125 (100)	103 (11)
1k	H	CN	207	7.5	35	438 (82)	205 (97)	116 (100)	103 (69)	102 (94)	5.7	41	322 (29)	219 (100)	116 (82)	103 (19)
2d	OMe	H	230	7.8	37	448 (8)	210 (53)	91 (12)	133 (12)	77 (100)	5.9	32	357 (9)	224 (18)	91 (100)	133 (12)
2j	Br	H	233	10.0	39	544 (8)	258 (10)	91 (11)	181 (0.5)	77 (100)	5.2	40	453 (2)	272 (3)	91 (100)	181 (4)
2k	CN	H	231	6.1	38	438 (34)	205 (50)	91 (67)	128 (8)	77 (100)	5.8	19	347 (25)	219 (26)	91 (100)	128 (1)

[1] temperature, °C, at which thermolysis was stopped

[2] time, min, at which the maximal intensity is reached during evaporation in MS (dT/dt = 40–50 deg/min)

[3] contribution of the component's TIC to the whole TIC of the sum spectrum (rel. error 10%)

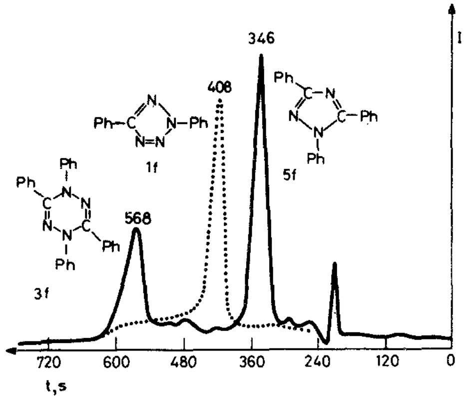


Fig. 4 HPL chromatogram of the product mixture of *1f* after Δm_1 (RP 18, flow 1 ml/min, MeOH (7% H_2O), detektim 270 nm)

be valid for assigning the HPLC signals. Disregarding the 1,2,3-triazoles, satisfactory results could be obtained.

In order to get another proof, the product mixture from the thermolysis of *1h* was separated into two homogeneous substances by means of thick-layer chromatography. They were identified as 1-(4-chlorophenyl)-3,5-diphenyl-1,2,4-triazole *(5h)* and 1,4-di-(4-chlorophenyl)-3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine *(3h)* (see Tables 2 and 3).

In accordance with the thermoanalytical curves, compound *2g* was heated up to 220° ($T_p + 13$) in a preparative amount (1 g; 4.17 mmol). Separation of the product mixture by column chromatography (silica gel, benzene as eluent) yielded two pure main products: 3,5-di-(4-fluorophenyl)-1-phenyl-1,2,4-triazole *(6g)* and 3,6-di-(4-fluorophenyl)-1,4-diphenyl-1,4-dihydro-1,2,4,5-tetrazine *(4g)*. The characteristic UV absorption maxima of the main products facilitate the interpretation of the HPL chromatograms (Table 2).

For the MS residue analysis after the first decomposition step, only the methods of multicomponent analysis were successful. The multivariant evaluation program SEKOS [9], the operating principles of which will be published elsewhere [10], is based on analysis of the sufficiently different evaporations of the components of a given multicomponent mixture. SEKOS analyses sets of ca. 100 mass spectra of the mixtures, obtained during an evaporation run, the addition of which gives the sum spectrum of the mixture (see Fig. 8). The analysis of individual fragment ion intensities, depending on time during the evaporation run, allows the assignment of these fragments to definite compounds. Moreover, SEKOS supplies the number of main components, and their percentage of the total mixture (i.e. the contribution of the total ion current, TIC, of the component to the whole TIC of the mixture sum spectrum), and calculates the mass spectra of the components.

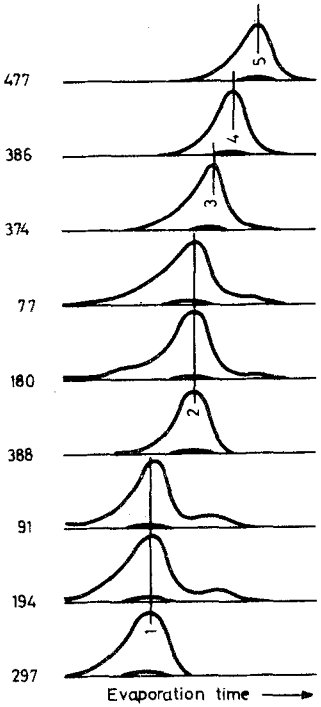


Fig. 5 Stepwise evaporation of five different substances from the product mixture of *1f* (Hewlett-Packard 5995 A)

The analysis of the intensity-time run in the case of the residue of *1f* after the first TG step revealed the presence of at least five compounds (Fig. 5). 76% of the whole TIC is due to only two of the five components, *5f* and *3f*. The TIC ratio of these components is 1.7 : 1 (48% : 28%), compared with the ratio of 2.2 : 1 estimated by HPLC. The agreement is satisfactory, for in the MS the smaller triazole molecules are ionized less frequently than the tetrazine molecules.

The component spectra calculated with SEKOS proved to be identical with the mass spectra of the authentic substances: *3f* and *5f* (Fig. 6). They can be explained through the main fragmentation routes of triazoles and tetrazines demonstrated in Fig. 7.

After testing of the SEKOS program in the described manner, further mixtures of thermolysis products were investigated. Analogous results were obtained. Figure 8 gives the sum spectra of the mixtures, while the mass spectra of the main products, evaluated from the analysis of these sum spectra, are listed in Table 3. The results confirm the decomposition routes presented in Fig. 3.

Furthermore, it becomes understandable that the mass losses in the first

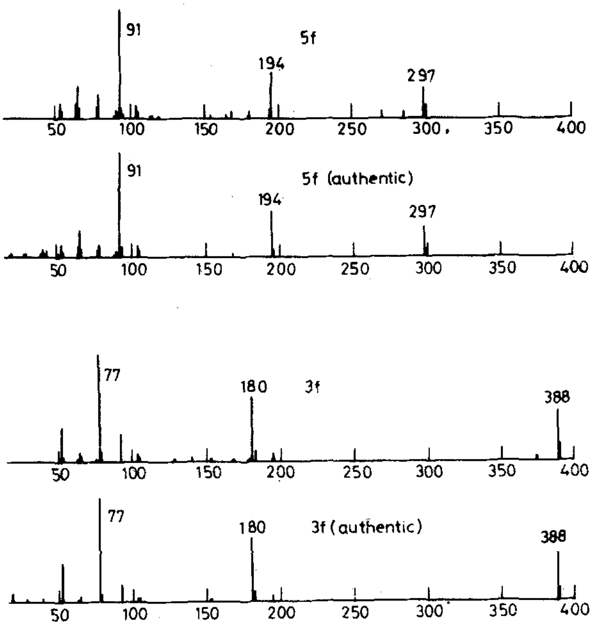


Fig. 6 Comparison of SEKOS-calculated mass spectra of the main products of *1f* with the authentic spectra

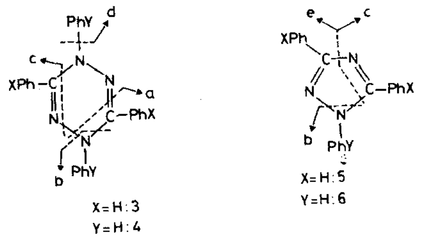


Fig. 7 Main fragmentation routes of the tetrazines (*3*; *4*) and triazoles (*5*; *6*)

decomposition step, exceeding the values calculated for 1 N_2, are caused by the evaporation of volatile compounds formed during the stabilization of the reactive diphenylnitrileimines. This also explains why the DTA curves after the strong exothermic peak look unspecific: evaporations, cracking and other conversions of the residue overlap.

Naturally, the volatile by-products could not be caught by means of the MS residue analysis. Therefore, the inert gas flow carrying the volatile species out of the

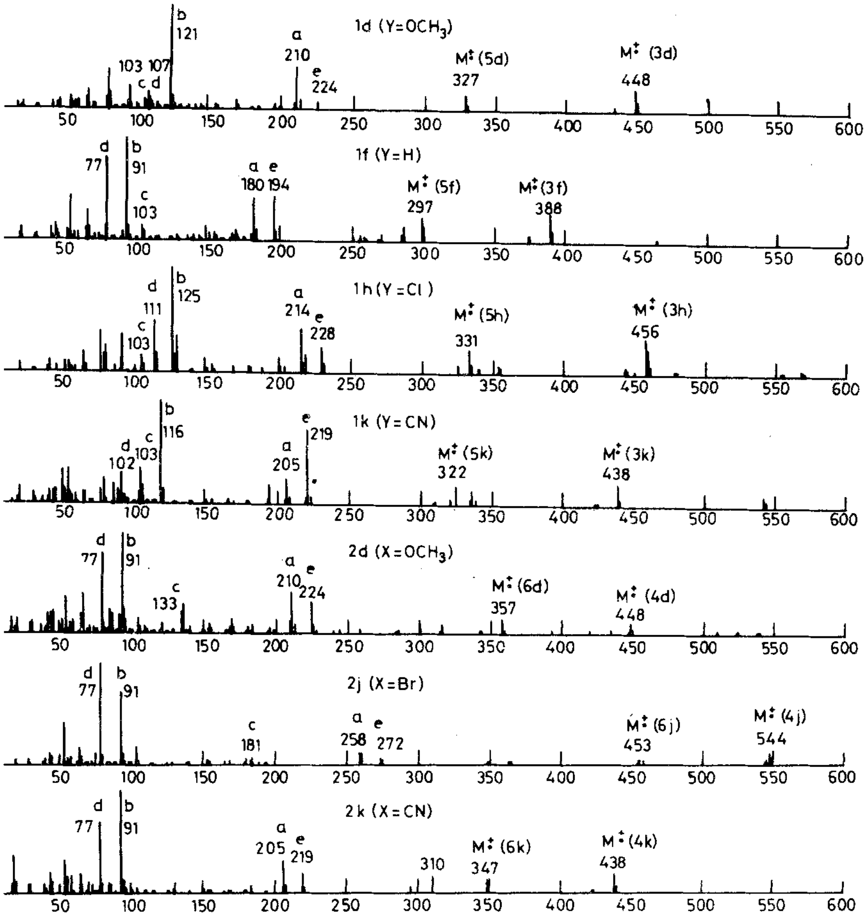
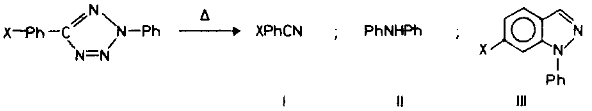


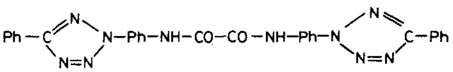
Fig. 8 Product mixture's sum spectra after the first TG step (structures of the fragments *a–e* in Fig. 7)

thermoanalyser was passed through a condensation tube (25°). MS analysis of the wall-coating in the case of the compounds *2a* and *2k* yielded the following compounds:



	I	II	III
2a :	M⁺˙ 146	M⁺˙ 169	
2k :	M⁺˙ 128	M⁺˙ 169	M⁺˙ 219

Obviously, the formation of volatile by-products is favoured if phenylnitrenes can easily be separated from the diphenylnitrileimines. If N-substituents of 2H-tetrazoles block the nitrene separation, mass losses should be expected which correspond only to nitrogen elimination from the tetrazole. In fact, the bis-tetrazole (7) loses $\Delta m_1 = 12.0\%$ in a well-separated TG step, which is in good accordance with the value calculated for 2 N_2 (10.1%).



(7)

References

1 M. Märky, H. Meyer, A. Wunderli, H. Heimgartner, H. Schmid and H. J. Hansen, Helv. Chim. Acta, 61 (1978) 1477.
2 V. Lohse, P. Leihkauf, Ch. Csongár and G. Tomaschewski, J. Prakt. Chem., in preparation.
3 S.-Y. Hong and I. E. Baldwin, Tetrahedron, 24 (1968) 3787.
4 Ch. Csongár, U. Klelin, V. Lohse, P. Leihkauf and G. Tomaschewski, Wirtsch. Pat. DDR, DD 220 151 Al (20. 7. 1983).
5 Ch. Csongár, M. Feist and G. Tomaschewski, Z. Chem., 27 (1987) 99.
6 A. Könnecke, P. Lepom and E. Lippmann, Z. Chem., 18 (1978) 214.
7 J. K. Stille and A. T. Chen, Macromolecules, 5 (1972) 377.
8 D. Schultze, Differentialthermoanalyse, Berlin, 1972.
9 L. Alder, R. Donau and Ch. Krüger, Ber. Zentralinst. Isotopen- u. Strahlenforsch. (Leipzig), N°-115 (1986) 135.
10 M. Feist, L. Alder and Ch. Csongár, to be published at ESTAC 4.
11 E. Bamberger, Ber. Dt. Chem. Ges., 34 (1901) 523.

Zusammenfassung — In der ersten Stufe der thermischen Zersetzung von diarylsubstituierten 2H-Tetrazolen aus der Schmelze werden unter Stickstoffeliminierung Diphenylnitrilimine gebildet. Sie reagieren trotz der drastischen Reaktionsbedingungen relativ selektiv und ergeben bevorzugt zwei Hauptprodukte — die entsprechend substituierten 1,2,4,5-Tetrazine und die 1,2,4-Triazole (zusammen mehr als 70%). Die Triazole werden gebildet, wenn günstige Bedingungen für eine Nitrenabspaltung aus den Nitriliminen vorliegen, was zu größeren Masseverlusten führt, als allein für N_2 zu erwarten wäre. Die nach der ersten TG-Stufe vorliegenden Produkte werden mit den Titelmethoden untersucht, insbesondere durch rechnergestützte MS-Analyse.

Резюме — На первой стадии термического разложения диарилзамещенных 2H-тетразолов происходит отщепление азота с образованием дифенилнитрилиминов. Несмотря на жесткие условия реакции, они относительно селективно реагируют с образованием двух основных продуктов: 1,2,4,5-тетразинов и 1,2,4-триазолов (их совместный выход составляет более 70%). Триазолы образуются в том случае, если предпочтительным является выделение нитренов из нитрилиминов. В связи с этим, наблюдаемые потери веса на первой стадии разложения намного выше ожидаемых при выделении только азота. Полученную на первой ТГ стадии разложения смесь продуктов исследовали, главным образом, масс-спектрометрическим методом.