THERMOANALYTICAL INVESTIGATIONS ON HETEROCYCLIC ORGANIC COMPOUNDS. PART IV. THERMAL DECOMPOSITION OF 1-BENZYL-1,2,3-TRIAZOLINO-4,5(N-PHENYL) DICARBOXIIMIDES

MAHMOOD M. BARBOOTI, DHOAIB A. AL-SAMMERRAI and
RASHAD M. AL-ANSARI

Petroleum Research Center, Council of Scientific Research, Jadiriyah, P.O. Box 10039, Baghdad (Iraq)

HASHIM T. AL-BADRI and ADIL F. ROOMAYA

Department of Chemistry, College of Science, Al-Mustansiriyah University, Baghdad (Iraq)

(Received 21 March 1984)

ABSTRACT

1-Benzyl-1,2,3-triazolinoimide derivatives are readily obtained by the action of benzyl-azides on *N*-phenylmaleimide and undergo loss of nitrogen, on heating, with the formation of the corresponding aziridine derivatives.

These aziridine derivatives undergo further decomposition on heating to give compounds of polymeric nature. This work comprises thermogravimetric and differential scanning calorimetric studies and the evaluation of kinetic parameters of the denitrogenation reaction using a computer program.

INTRODUCTION

Thermoanalytical techniques are gaining much interest in the study of organic compounds referring to their stability, structure and polymorphorism, i.e., physical and chemical transitions [1–9]. The action of substituted benzylazides on *N*-phenylmaleimide, in ethyl acetate, was found to proceed via 1,3-dipolar cyclo-addition to yield the corresponding triazolinoimide adducts [10]. These compounds are chemically interesting as they consist of two fused five-membered rings, which suggests the study of the influence of the imide ring on the thermal behaviour of the *N*-substituted triazoline ring. The effect of substituted benzyl derivatives on the thermal stability of the triazolino ring is also studied throughout this paper.
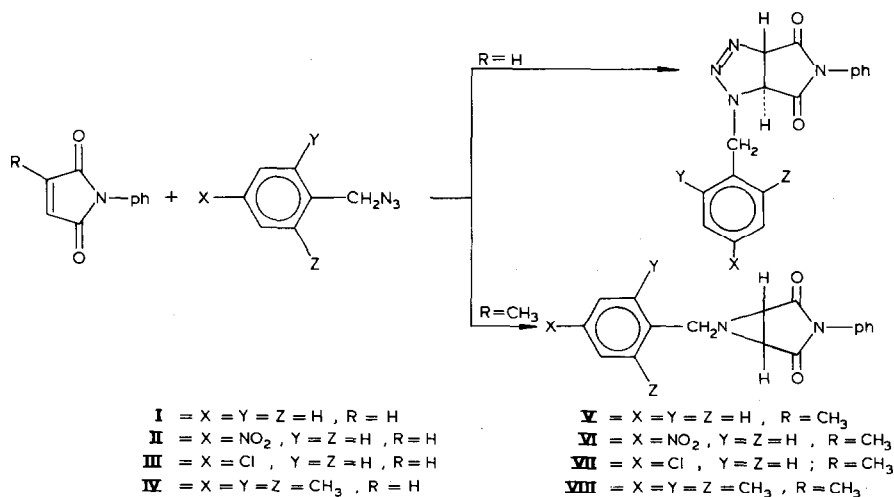
EXPERIMENTAL

Preparation

The general reaction of substituted benzylazides with *N*-phenylmaleimide and *N*-phenyl citraconimide was conducted by heating a solution of the imide and the azide, respectively, in a suitable solvent at reflux temperature for 18–24 h [10].

Thermal analysis

The TG, DTG and DSC measurements were carried out on a Heraeus TA-500 thermal analyser. For TG experiments 3–7-mg samples were placed in platinum crucibles and heated at a rate of 20° min^{-1} under static (air) and dynamic nitrogen atmospheres. For the DSC experiments the sample holders were aluminium dishes with silica as the thermal reference material. The samples were heated at 10°C min^{-1} under static and nitrogen atmospheres.

RESULTS AND DISCUSSION

The TG and DTG curves of the compounds **I–VIII** are shown in Figs. 1 and 2. The corresponding DSC curves are shown in Figs. 3 and 4. The characteristic decomposition reaction appears to be the loss of a nitrogen molecule from the triazoline ring. The decomposition temperatures, as well
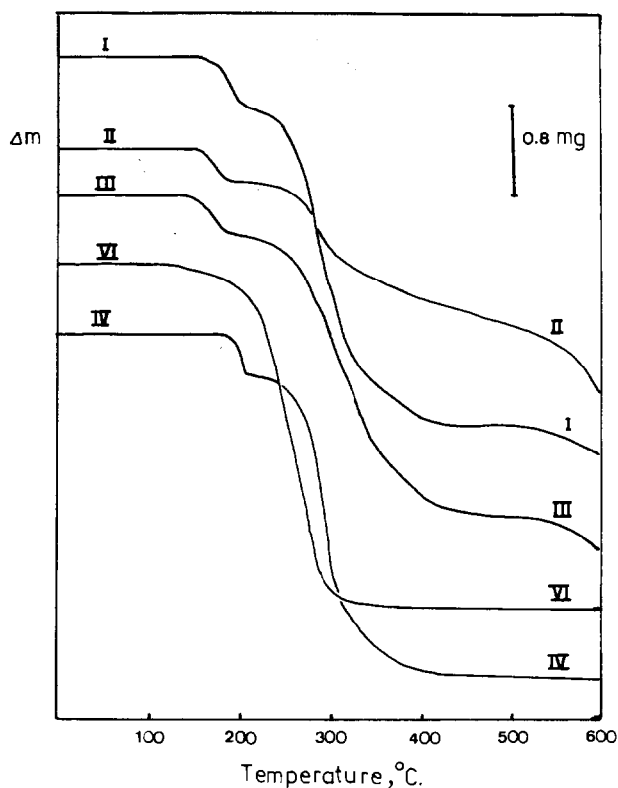

I = X = Y = Z = H , R = H	**V** = X = Y = Z = H , R = CH$_3$
II = X = NO$_2$, Y = Z = H , R = H	**VI** = X = NO$_2$, Y = Z = H , R = CH$_3$
III = X = Cl , Y = Z = H , R = H	**VII** = X = Cl , Y = Z = H ; R = CH$_3$
IV = X = Y = Z = CH$_3$, R = H	**VIII** = X = Y = Z = CH$_3$, R = CH$_3$

Scheme 1

Fig. 1. TG curves of compounds **I–IV** and **VI**. DTG curves are not shown as they add no further information.

as the reaction intervals, have been found to be dependent on the substituents at the *para* position in the benzyl ring.

The quantitative evaluation of the TG curves is given in Table 1. The

TABLE 1

Denitrogenation data of triazolinoimides [a]

Compound	MW	N₂ lost		Temp. range (°C)	Maximum rate temp. (°C)
		% Calc.	% Found		
I	306	9.1	11.3	156–209	185
II	351	7.97	8.57	157–210	185
III	340.5	8.2	9.23	147–218	188
IV	348	8.4	11.87	180–220	205
V	320	8.75	2.5	113–175	153
VI [b]	365	7.67	1.4	82–120	95
VII [b]	354.5	–	–	–	–
VIII [b]	362	–	–	–	–

[a] The figures are extracted for TG experiments carried out under nitrogen atmosphere.
[b] Nitrogen is lost during preparation and storage.

difference between the practical and the calculated percentages of nitrogen loss may be attributed to the immediate decomposition of the product, i.e., the denitrogenation reaction step overlaps at the end with the following decomposition step as the DTG signal did not return to the baseline.

The marked difference between the values of the nitrogen loss for compounds V and VI may be attributed to the low denitrogenation temperatures of the corresponding triazolino adducts which might lose nitrogen, even during storage. Similar observations were noticed in the decomposition of pyrazolinoimides [7].

The denitrogenation begins slowly in the solid state and proceeds at a faster rate after melting, as noticed visually at the Kopfler hot bench apparatus. The DSC curves (Figs. 3 and 4) indicated that the reaction is exothermic regardless of the nature of the atmosphere used. The exothermic character is often a characteristic of a thermal decomposition reaction which involves the removal of diatomic gases [7,11]. Mechanistically, it seems that the pyrolysis of the triazolinoimides proceeds in a similar manner to that of the pyrazolinoimides and pyrazolinodiazipines [12], i.e., the biradical is
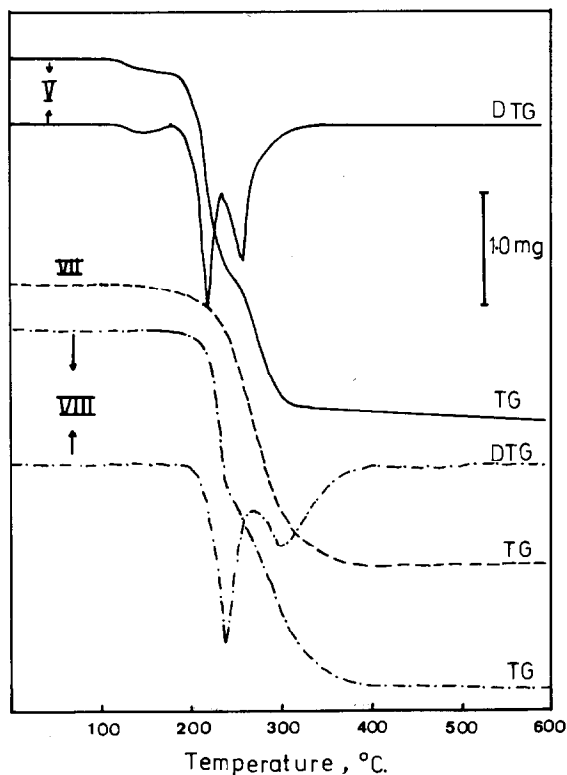

Fig. 2. TG and DTG curves of compounds **V**, **VII** and **VIII**. DTG curves of compound **VII** is omitted as it adds no further information.
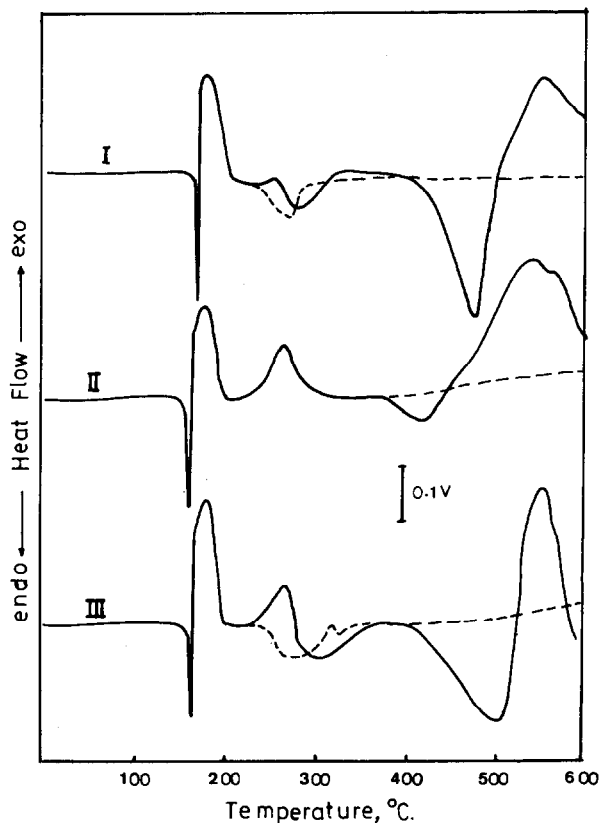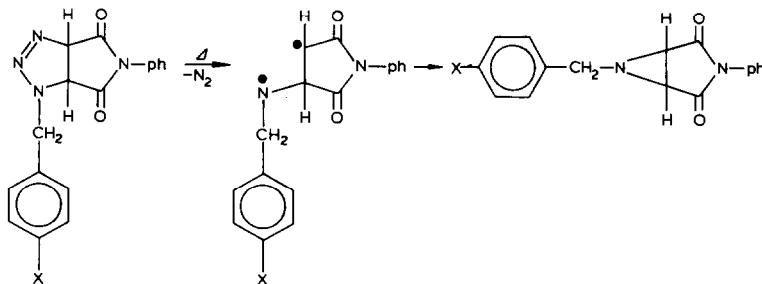
Fig. 3. DSC curves of compounds I–III: (———) under air atmosphere; (– – –) under nitrogen atmosphere. Compound **IV** has a DSC signal typical of that of compound.

formed as an intermediate stage (cf. Scheme 2).

From Scheme 2, we emphasize that the pyrolysis of the triazolinoimides results in the formation of the corresponding aziridines as a primary product prior to the formation of any other expected products, e.g., amines or imines. This can be confirmed by the data extracted from the TG curves of triazolinocitraconimide. The methyl group lowers the reaction temperature

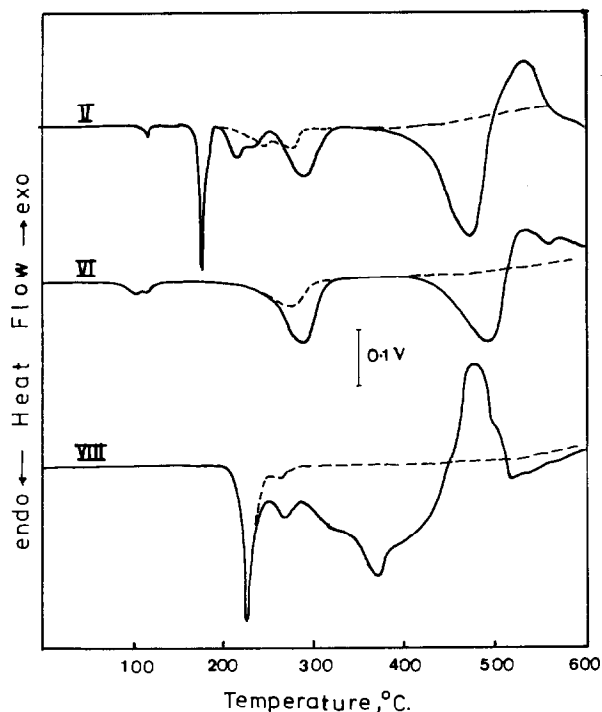Scheme 2. Mechanism of the denitrogenation.

Fig. 4. DSC curves of compounds V–VIII: (———) under air atmosphere; (– – –) under nitrogen atmosphere.

significantly through the $(+I)$ inductive effect which stabilizes their aziridine derivatives. The destabilization due to the methyl group is enhanced by the substituents at the *para* position in the benzyl structure (cf. Table 1). This might explain the ready removal of nitrogen from the triazolinocitraconimide derivatives.

In an attempt to establish a kinetic basis for the effect of substituents on the decomposition of compounds **I–III**, separate TG experiments were performed. Samples weighing 6–8 mg were heated at 10 K min^{-1}, and the curves were recorded with modified sensitivity and a widened temperature

TABLE 2

Kinetic parameters of the denitrogenation reactions

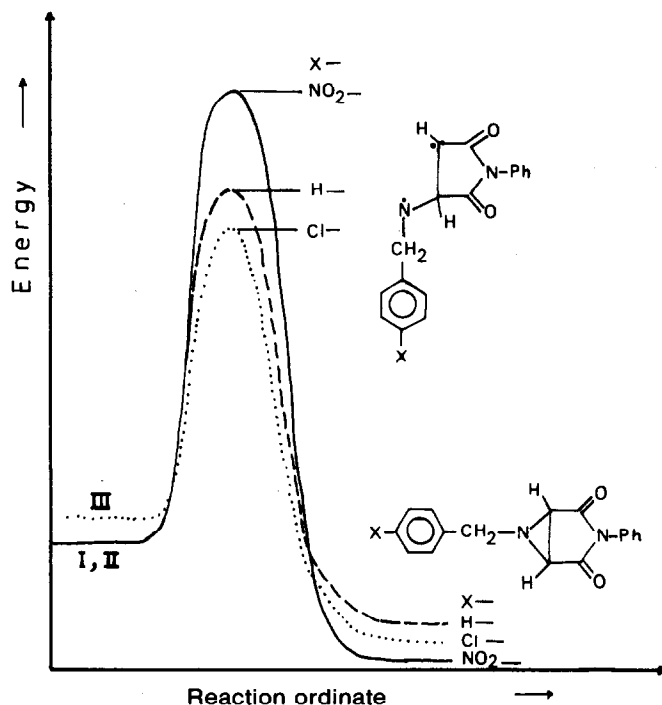| Compound	Activation energy E_a (kg mol^{-1})	Reaction order, n	Pre-exponential factor, log Z	Correlation coefficient
I	350	2.1	42.5	0.99876
II	460	3.9	55.2	0.98959
III	310	3.1	39.7	0.99080

Fig. 5. Chemical kinetics of the denitrogenation reaction. The order of reactants and products refers to the thermal stability. The order of the intermediates refers to the activation energy.

scale. A computer program [13] was employed to carry out the calculations for the estimation of reaction order, n, activation energy, E_a, and the pre-exponential factor, expressed as $\log Z$. The kinetic parameters, thus obtained, are listed in Table 2. It is clear from the table that the activation energy of the decomposition of the compound 1-benzyl-1,2,3-triazoline-4,5-(N-phenyl)dicarboxiimide (I) lies between those of the p-chloro and the p-nitro derivatives. Such a trend in activation energy values could be explained by taking into consideration the stability of the transition state, i.e., the corresponding biradicals of compounds I–III (cf. Fig. 5). The presence of the nitro group at the *para* position stabilizes the aziridine produced through the $\pi-\pi$ conjugation. In contrast, the presence of the chloro substituent stabilizes the biradical by supplying π-electron density to conjugated system through the $(+R)$ effect. It is worthwhile mentioning that the compound 2,4,6-trimethylbenzyltriazolinomaleimide loses nitrogen at a relatively higher temperature (183–225 °C). The stability of the triazolino ring, in this case is gained from the presence of two methyl groups at the *ortho* position exerting a combined $(+R)$, $(+I)$ effect. Additionally, the methyl group at the *para* position reinforces these effects.

THERMAL DECOMPOSITION OF AZIRIDINES

The thermal decomposition of the aziridinomaleimide derivatives corresponding to compounds I–V were generally similar to the decomposition of the aziridinocitraconimides (VI–VIII).

The melting points of the aziridino derivatives (I–IV) could not be determined from the thermogram since the ambient temperature (denitrogenation temperature of the corresponding triazolino derivative) is higher than their melting points, i.e., these derivatives already exist in the molten state. Two principal features can be noticed from the thermograms of the aziridines. The first commences from the tail of the denitrogenation and ends at 380–400 °C, while the second succeeds the first and continues until the end of the heating program (600 °C). The second feature (Figs. 3 and 4), however, is atmosphere dependent, as the signals in this feature disappear in the thermograms recorded under nitrogen atmosphere. The first stage represents the cleavage of the aziridino ring by a series of steps including the probable isomerization into the amine structure (Scheme 3). Also, it com-
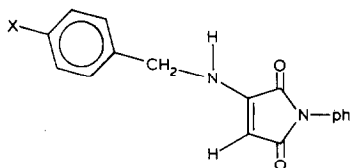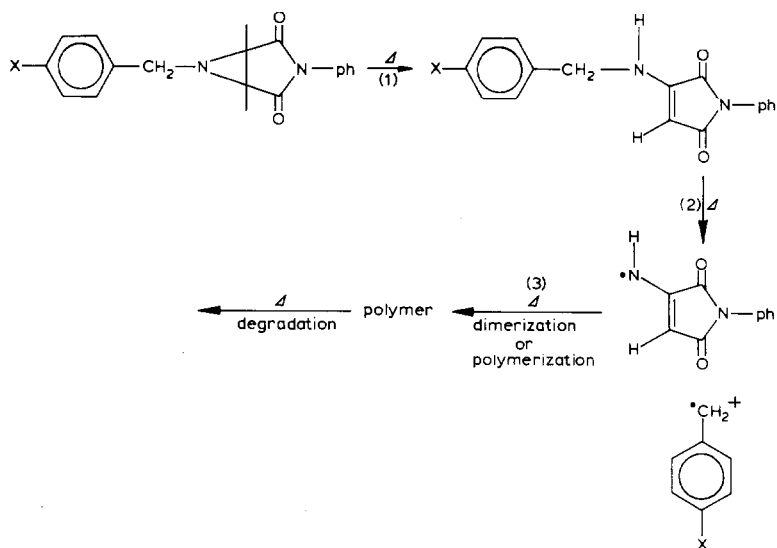

Scheme 3

prises the degradation of the amine derivative produced to give the benzyl radical and the radical of the remaining part of the molecule, which could dimerize, in addition to the possibility of the polymerization of the amine produced. The resulting polymer undergoes degradation by an atmospheric dependent route because of the ability of atmospheric oxygen in retarding the degradation in the last stages, i.e., oxidizable species are formed during the course of the decomposition. The *para* substituent greatly influences this stage of the decomposition. The beginning of the process is slightly exothermic in the unsubstituted compound and becomes endothermic later on (cf. Fig. 3). It appeared exothermic in the nitro derivative even under inert atmosphere, while the chloro derivative retained the thermal behaviour of the unsubstituted compound. The decomposition of the aziridine can, therefore, be described by Scheme 4.

Step (1) of this mechanism can be a consequence of the good thermal stability shown by these compounds, where the amine is more stable than the corresponding aziridine derivative [14]. The percentage of weight losses given by the *p*-nitro derivative (II), and the two-step degradation of compounds V–VIII support the feasibility of step (2). Step (3) may be supported by the occurrence of double bond containing species and the exothermic nature of

Scheme 4

the change, in addition to the thermal environment which aids polymerization.

REFERENCES

1 H.M. Frey and S.P. Lodge, J. Chem. Soc., Perkin Trans. 2, (1979) 1463.
2 S. Zeman, Thermochim. Acta, 41 (1980) 199.
3 A. Burger and R. Ramberger, Mikrochim. Acta (Wien), I (1981) 217.
4 R.A. Bolivar, E. Cotte, C. Perez and C. Rivas, Thermochim. Acta, 45 (1981) 125.
5 V. Cerda, E. Casassas and F. Borrull, Thermochim. Acta, 57 (1982) 195.
6 C. Gandolfo and D. Grasso, Thermochim. Acta, 65 (1983) 239.
7 H.T. Al-Badri and M.M. Barbooti, Thermochim. Acta, 53 (1982) 45.
8 M.M. Barbooti, H.T. Al-Badri and A.F. Roomaya, Thermochim. Acta, 70 (1983) 347.
9 M.M. Barbooti and D.A. Al-Sammerrai, Thermochim. Acta, 76 (1984) 221.
10 H.T. Al-Badri, A.F. Roomaya and Z.S. Salih, in preparation.
11 M.M. Barbooti and F. Jasim, Thermochim. Acta, 16 (1976) 402.
12 P. Gesche, F. Klinger, J. Streith and H. Straub, Tetrahedron Lett., 21 (1980) 4507.
13 F. Jasim, M.M. Barbooti and K.I. Hussain, Thermochim. Acta, 58 (1982) 289.
14 W.I. Awad, S.M.A.R. Omran and F. Nagieb, Tetrahedron, 19 (1963) 1591.