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THERMOANALYTICAL INVESTIGATIONS ON HETEROCYCLIC ORGANIC COMPOUNDS. PART I. THERMAL DECOMPOSITION OF PYRAZOLINOIMIDES

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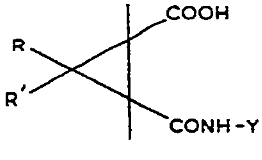
ABSTRACT

Pyrazolinoimides undergo denitrogenation reaction upon heating to form the cyclopropane derivatives and the corresponding olefins They are studied by dynamic TG, DTG, DTA and DSC techniques The enthalpies and kinetic parameters are evaluated Further decomposition of the compounds led to carbon, and in some cases, polymeric products are suspected to be formed The fluorene derivatives behave differently and undergo irreversible isomerization in the melt prior to decomposition Practical mechanistic steps are postulated in order to explain the formation of the decomposition, rearrangement and isomerization products during thermal treatment

INTRODUCTION

Little is known about the pyrolysis of pyrazolines. Several imidopyrazolines were prepared by Awad et al. [1,2] by the action of, for example, diazomethane on *N*-phenyl maleimide. They [1] carried out the pyrolysis of Δ^1-pyrazoline-4,5-(*N*-phenyl)-dicarboximide [Scheme 1(I)], under normal and reduced pressures, but without thorough investigation of the results. Jaz and Millett [3] synthesized new pyrazolines by the reaction of *N*-phenyl maleimide with some other diazoalkanes. They claimed that the pyrolysis of these pyrazolines gave, after extraction with petroleum ether, three distinct compounds, namely, Δ^2-pyrazoline, cyclopropane derivatives, and the corresponding olefins. On hydrolysis, the cyclopropanes (the minor product they obtained) in alcoholic potassium hydroxide solution gave 70% of the corresponding 3-(*N*-aryl) carboxamide cyclopropane-1-carboxylic acid.



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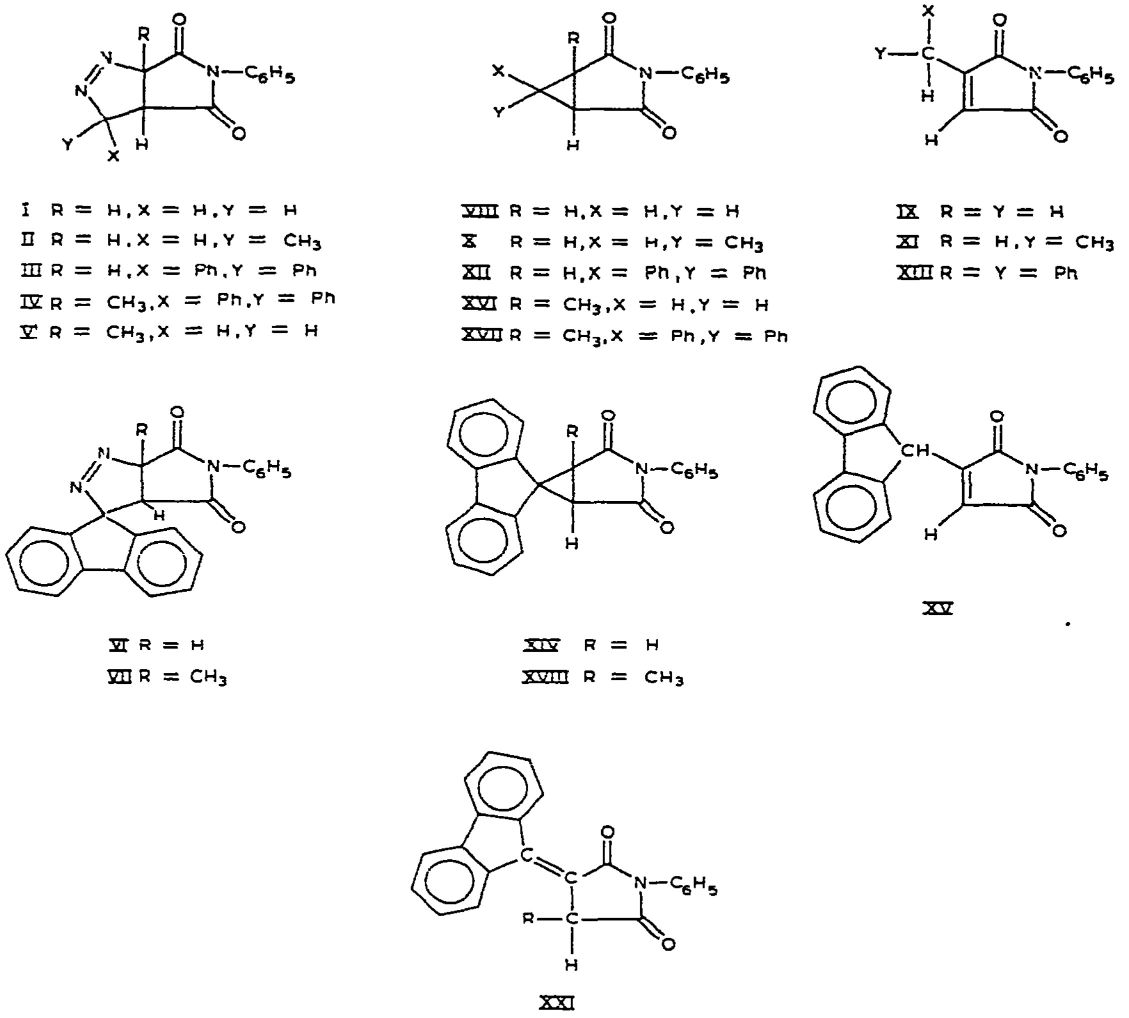


Scheme 1. Structural formulae of the pyrazolinoimides and their pyrolysis products

The available literature indicates that the cyclopropane carboxamides to which these compounds belong have important biological activities but the data are usually contained within patents [4].

It is the aim of the present work to study the thermal behaviour of some new pyrazolines which have been prepared recently [5] together with the pyrazoline of *N*-phenyl maleimide using thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC). These attempts are carried out to investigate:

(i) the factors and parameters affecting the stability of the pyrazolinoimides;
(ii) the best conditions that permit the formation of the cyclopropane derivatives as the major products;
(iii) the effects of the different substituents at the imidic ring as well as at the C-3 of the pyrazoline ring on the thermal stability of the pyrazoline and the cyclopropane derivatives.

EXPERIMENTAL

Preparation

The compounds studied were prepared by the action of diazoalkanes, namely, diazomethane, diazoethane, diphenyl diazomethane, and diazofluorene, on *N*-phenyl maleimide and *N*-phenyl citraconimide in diethyl ether at 0°C [5]. The structures of the Δ^1-pyrazolines were established by elemental analysis (Alfred Bernhardt Microanalytical Laboratory, Mulheim, Germany), as well as from spectral evidence [5].

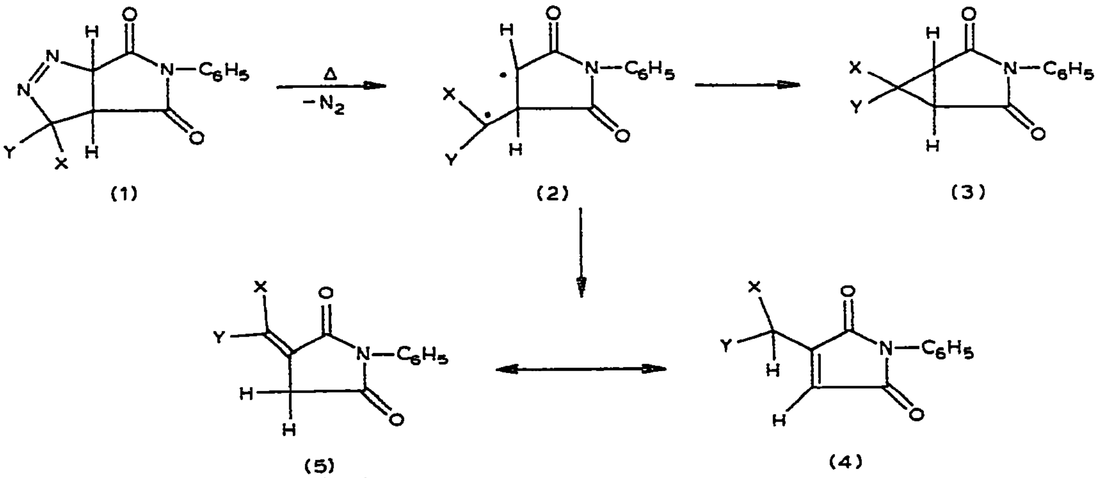
Thermal analyses

The simultaneous TG, DTG, and DTA measurements were carried out on a MOM derivatograph (Hungarian Optical Works) under nitrogen (99.9996%) flowing at a rate of 30 ml min^{-1}. The dynamic atmosphere was guaranteed by a special kit supplied as part of the MOM gas titrimetric unit. Samples weighing 50–100 mg were placed in small platinum crucibles and heated at a rate of 10°C min^{-1}. The reference material for the DTA measurements was α-Al_2O_3 which was already heated to 1500°C.

The DSC measurements were carried out in a Mettler TA 3000 system [6]. The sample weights were in the range 2–5 mg. The reference cell was left empty. The sample and the reference cells were sealed by a special kit supplied by the manufacturer and placed on the heating elements with the aid of forceps. The heating was carried out at a rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

The thermoanalytical curves (TG, DTG, and DTA) of compounds (I)–(VII) are shown in Figs. 1–7, respectively. The results of the quantitative evaluation of the TG



Scheme 2 Mechanism of the denitrogenation

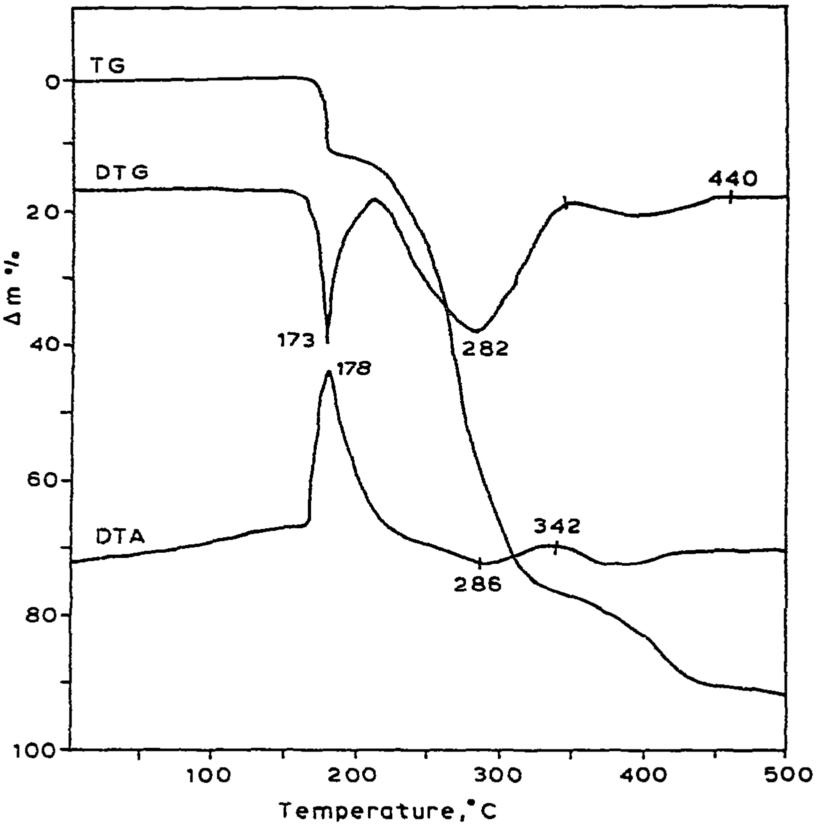


Fig 1 Thermoanalytical curves TG, DTG, and DTA of compound (I)

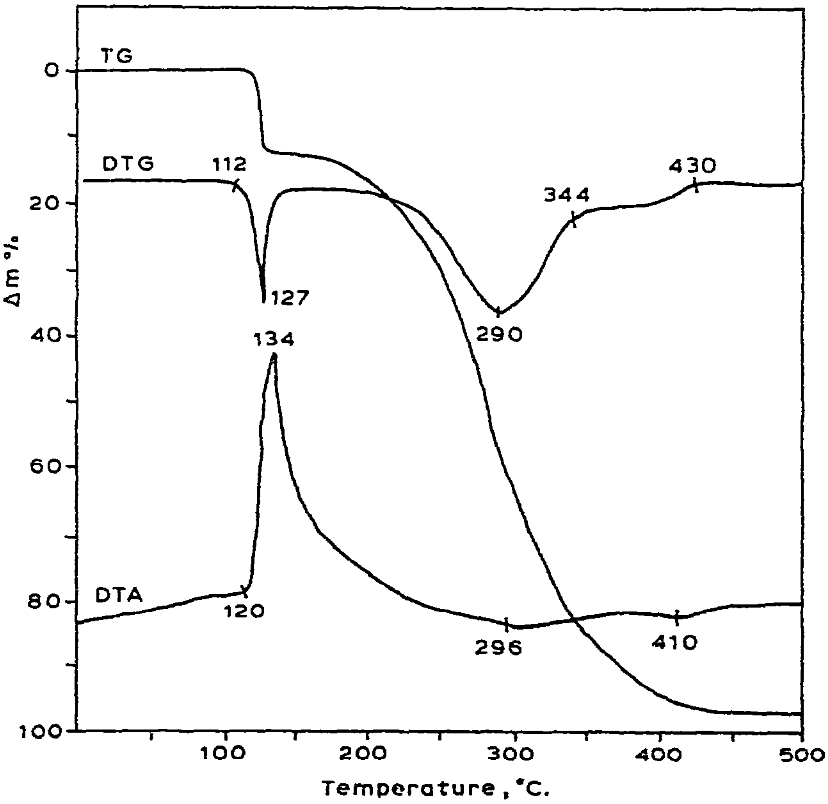


Fig 2 Thermoanalytical curves TG, DTG, and DTA of compound (II).

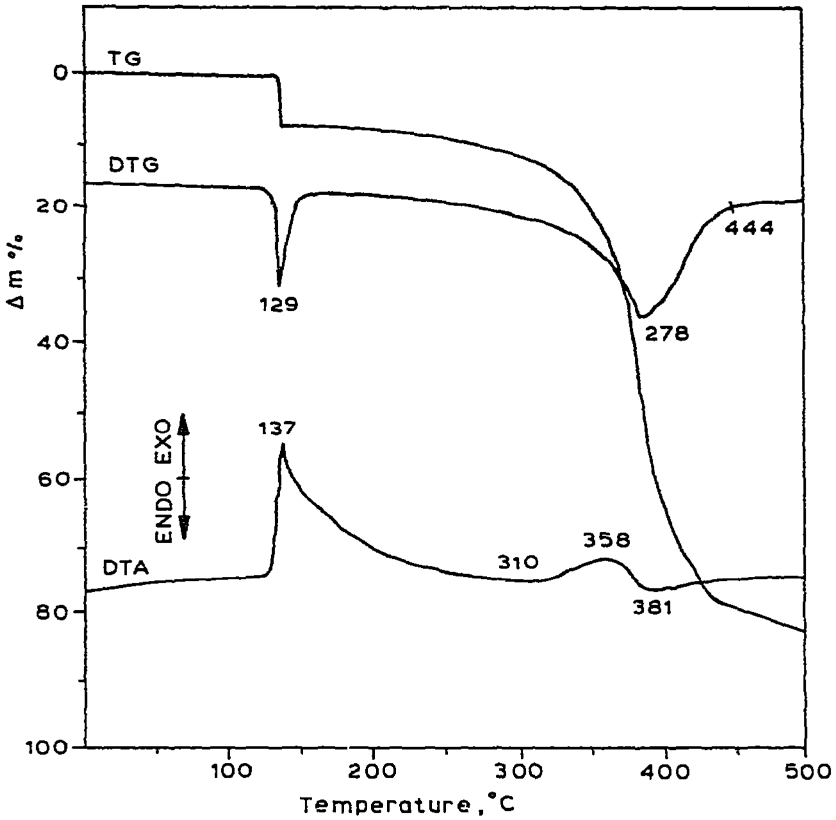


Fig 3 Thermoanalytical curves TG, DTG, and DTA of compound (III)

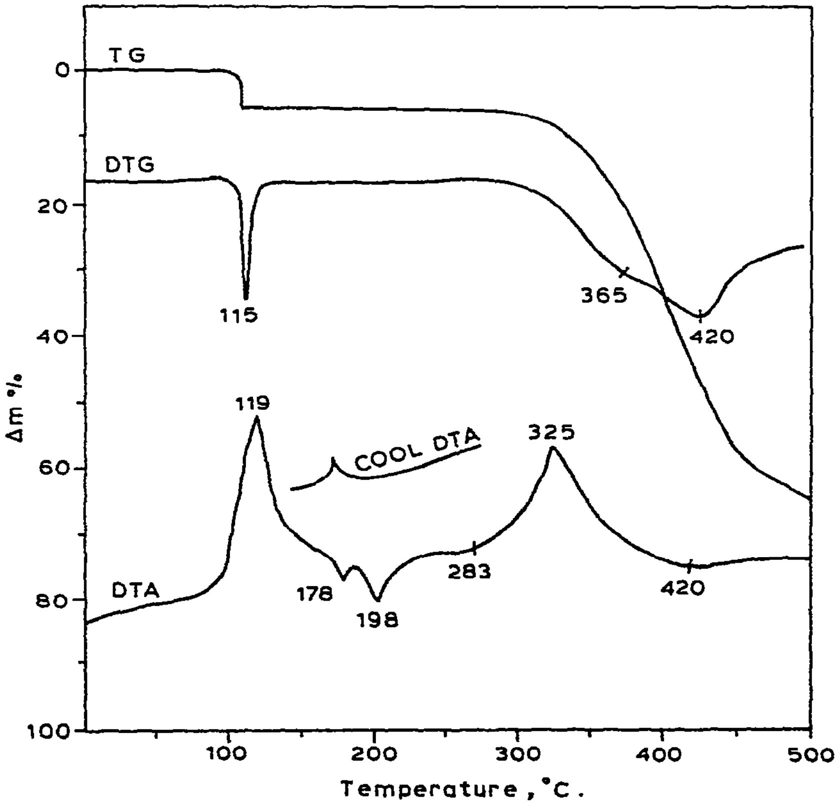


Fig. 4. Thermoanalytical curves TG, DTG, and DTA of compound (IV).

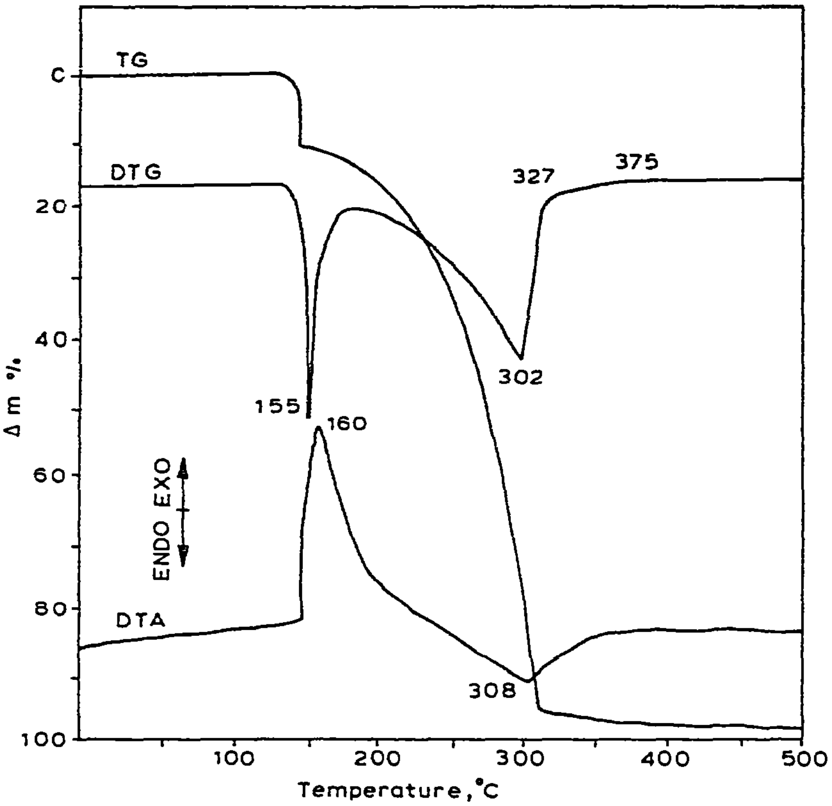


Fig 5 Thermoanalytical curves TG, DTG, and DTA of compound (V).

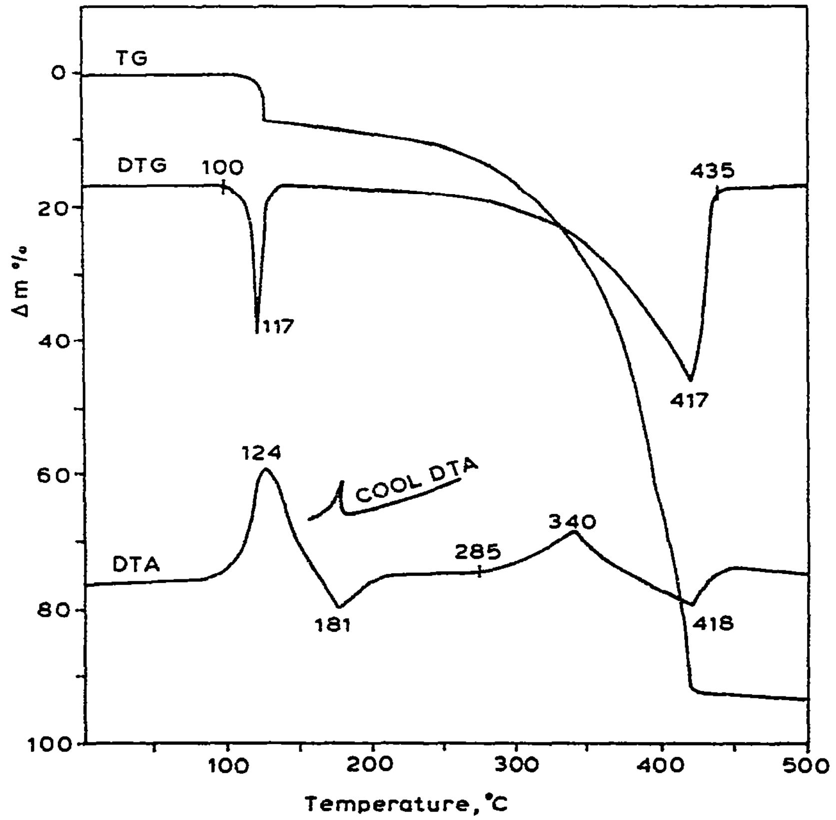


Fig 6. Thermoanalytical curves TG, DTG, and DTA of compound (VI)

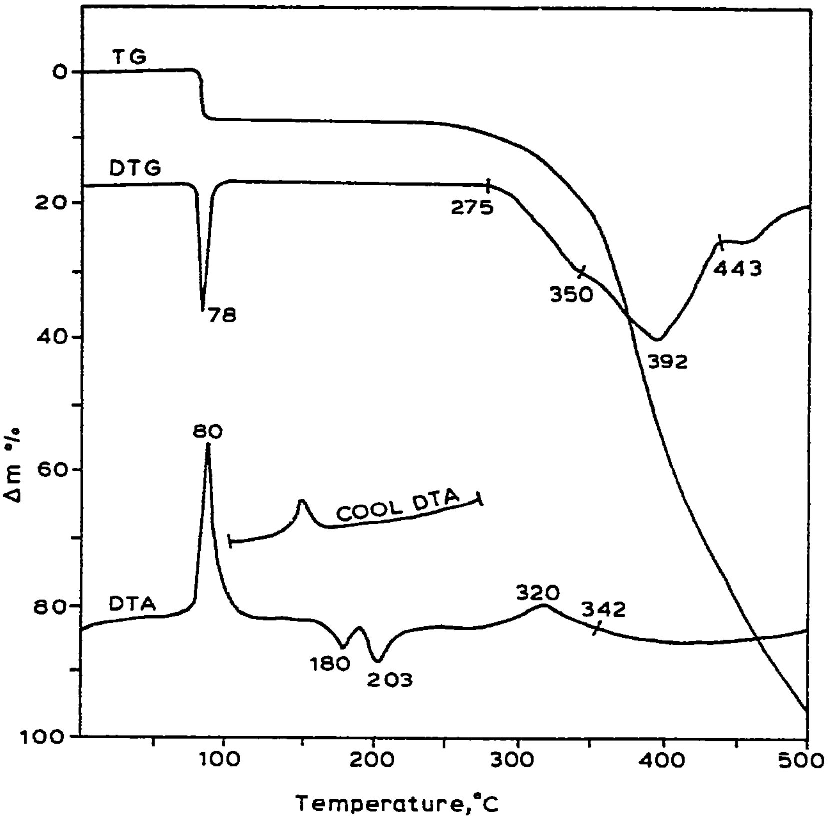
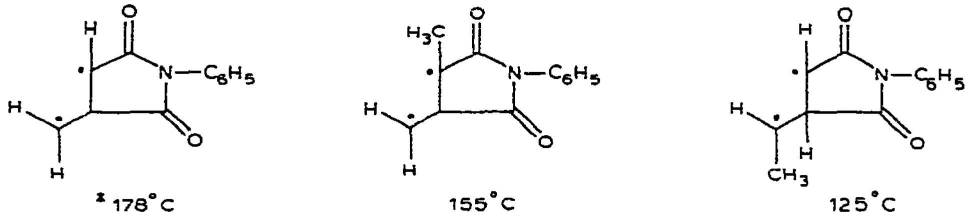


Fig 7 Thermoanalytical curves TG, DTG, and DTA of compound (VII)

curves are given in Table 1. The IR spectral data of some selected pyrazolinoimides and their decomposition products are listed in Table 2. The first decomposition reaction is the loss of a nitrogen molecule per molecule of these compounds. The agreement of the practical results of the N_2 lost with that predicted by calculation (Table 1) rules out the possibility of Δ^2-pyrazoline formation under the present conditions. This is in contrast to the report of Jaz and Millett [3]. Therefore, the only two products are the cyclopropane derivative and the corresponding olefin (Scheme 2).

The formation of compounds 3 and 4 or 5 seems to be straightforward from a mechanistic standpoint, provided that the biradical intermediate 2 be postulated (Scheme 2). However, a similar mechanism was reported by Streith and co-workers [7] for the thermal activation of pyrazolinodiazipines. In order to support the biradical formation mechanism, the denitrogenation temperature of compound(I) may be compared with that of (II) and (V). The methyl group lowers the reaction temperature significantly through the $(+I)$ inductive effect which stabilizes the cyclopropane derivative produced. Moreover, the methyl group at C-3 has a greater effect on lowering the temperature than that at C-5 [compound (II)], which is consistent with the expected stability of the biradical formed from compounds (II) and (V), Scheme 3.



Scheme 3 Denitrogenation temperatures

Pyrolysis of Δ^1-pyrazolinocitraconimide gave only structures of type 3, and no isomers of type 4 and 5 were isolated. The relative yield of 3 and 4 or 5 can be attributed to the bulk of the groups attached to the C-3 in the pyrazoline ring. When bulky groups are present, e.g. ($R = R' = Ph$), the angle between these two groups (α) would be larger than 109°28′ and consequently the opposite angle (β) would be necessarily smaller, i.e. sufficiently small to stabilize the cyclopropane [8].

The discrepancy in the denitrogenation temperatures can be explained in terms of (1) steric interference, and (2) electronic factors. In the case of the pyrazolinomaleimides, the steric interferences of the substituents at C-3 in the pyrazoline ring is the only factor that affects the pronounced decrease of the reaction temperature, starting from the unsubstituted pyrazoline down to the 9-fluorene derivative, whereas in the case of the pyrazolinocitraconimides, both factors influence the denitrogenation temperature, i.e. the action of the methyl group on the stabilization of the cyclopropane ring in the product, and the steric hindrance by the bulky groups at the C-3 of the pyrazoline ring. This is consistent with the denitrogenation temperature of the pyrazolinocitraconimide derivatives being lower than that of the corresponding pyrazolinomaleimides.

Estimation of the m.p. by the Kofler hot bench indicated that melting is accompanied by bubbling of some gas. In most cases the melting point is identical to

TABLE 1

Quantitative evaluation of the TG curves regarding the denitrogenation reaction

Compound	Temp. [a] (°C)	N_2 lost (%)		Mol wt.
		Found	Calcd	
I	173 [b]	13.1	13.02	215
II	127	12.0	12.22	229
III	129	7.8	7.63	367
IV	115	7.6	7.67	365
V	155	12.3	12.3	229
VI	117	7.5 [c]	7.34	381
VII	78	6.5 [c]	7.38	379

[a] The temperature at the maximum of the DTG peak

[b] This confirms the data reported by Awad et al [1].

[c] Nitrogen can be lost partially during recrystallization.

Table 2

IR spectral data of the pyrazolinoimides and their cyclopropane derivatives

Compound No	$\nu_{C=O(asym)}$ (cm^{-1})	$\nu_{C=O(sym)}$ (cm^{-1})	$\nu_{N=N}$ cm^{-1}	C–H in-plane deformation	C–H out-of-plane deformation
I	1750 s	1760 s	1570 s	1400 s, 1280 s, 1140 s, 1060 m, 1040 s, 990 s	890 s, 870 s, 830 m, 740 s, 715 s, 692 s
II	1752 s	1700 s	1752 m	1470 s, 1360 s, 1260 m, 1160 s, 1140 s, 990 m	880 s, 810 m, 730 s, 790 s
III	1765 m	1690 s	1570 m	1370 s, 1250 m, 1170 s, 980 w, 950 m, 915 m	890 s, 780 m, 760 s, 733 s, 695 s, 685 s
V	1786 s	1724 s	1555 m	1380 s, 1280 s, 1220 s, 1150 s, 1050 s, 915 s	870 s, 800 w, 760 m, 730 s, 690 s
VI	1800 s	1700 s	1570 s	1370 s, 1750 s, 1220 s, 1140 s, 1010 m, 930 s	880 s, 785 m, 755 s, 730 s, 695 s, 680 s
XIV	1790 m	1700 s		1365 s, 1250 m, 1205 s, 940 m	895 m, 760 s, 750 s, 735 s, 725 m, 690 s
XVI	1730 m	1680 s		1470 s, 1190 s, 1125 s, 920 m	892 s, 810 m, 770 s, 760 s, 728 m, 700 s
XVII	1750 m	1666 s		1350 s, 1180 s, 1100 s, 920 m	825 m, 777 s, 740 s, 705 s, 688 m
XVIII	1745 s	1650 s		1350 s, 1250 m, 1105 s, 1100 m	895 s, 860 s, 770 s, 730 m, 715 m, 692 s

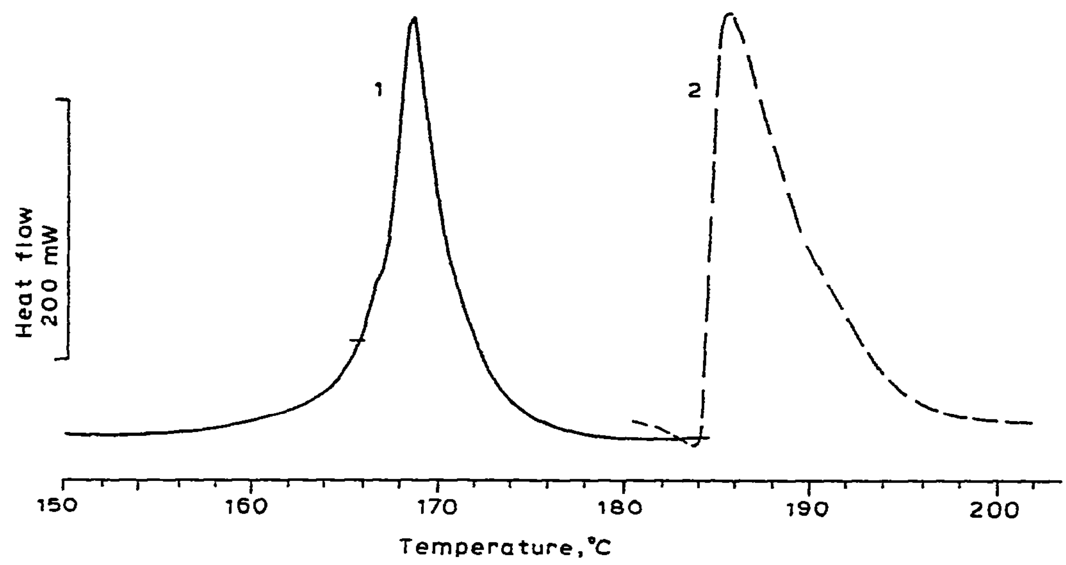


Fig 8 Dynamic DSC curves of the denitrogenation reaction of compounds V (1) and I (2)

the denitrogenation temperature determined by the TG curves (Fig. 1). In other cases some descrepancy appeared and the DSC curves of Δ^1-pyrazoline-2,3-(*N*-phenyl)dicarboximide (Fig. 8) indicate an incomplete endothermic process preceding the denitrogenation exotherm. The endotherm refers to melting of the compound. Such findings may assume that the denitrogenation is facilitated by the melting, and consequently it is not a first-order reaction. The DSC curve of compound Δ^1-pyrazoline-2,3-(*N*-phenyl)dicarboximide was used for the estimation of the kinetic parameters of the reaction. The mini-computer of the Mettler TA 3000 system is supplied with a built-in program by which the extent of the reaction, α, is calculated as a function of time for some preselected temperatures and plotted on a single chart, according to the method of Altorfer [9]. The plots could be considered as isothermal plots. The results are displayed graphically in Fig. 9. The kinetic plots are shown for the temperatures 165, 170 and 175°C, since the peak temperature, as evaluated by the system is 170.7°C. The reaction order (n), activation energy (E_a), and the rate constant expressed as ln K_0 are, respectively, 1.63, 759.33 kJ mole and 203.49.

The value of the reaction order confirms the facilitation of the denitrogenation by melting. The enthalpy of the denitrogenation reaction was estimated, for Δ^1-pyrazoline-4-methyl-2,3-(*N*-phenyl)dicarboximide and Δ^1-pyrazoline-2,3-(*N*-phenyl)dicarboximide, from the DSC curves and found to be 80.85 and 92.03 kJ mole^{-1}, respectively. The values are close to each other, within experimental error although the difference in the reaction temperatures is considerable. This may be further evidence for the validity of the stability of the free radicals during the reactions.

The TG curves (Figs. 1 and 2) indicate that the next decomposition reactions are dependent on the nature and the degree of substitution at the pyrazoline ring. In general, the cyclopropyl citraconimides showed greater thermal stability than the

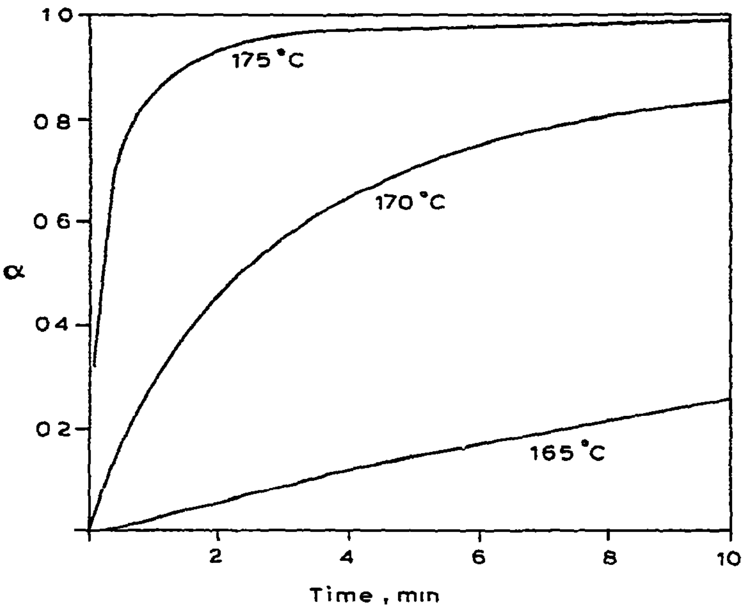


Fig 9 Kinetic plots of the denitrogenation reaction of compound (V)

cyclopropyl maleimides, as indicated by the faster rate of the initial decomposition of the latter compounds. From the TG, DTG, and DTA curves (Figs. 1–3), it can be seen that the decomposition of compounds (XVI), (XVII), and (XVIII) proceeds directly to the final pyrolysis product, carbon, while the decomposition of compounds (VII)–(XV) proceeds via an intermediate product at the final stages. The cooled products at these intermediate stages were mixtures of carbon with some products, for which the spectral identification was difficult, due to the carbon. The formation of the citraconimide olefins (IX), (XI), (XIII) and (XV) from the de-

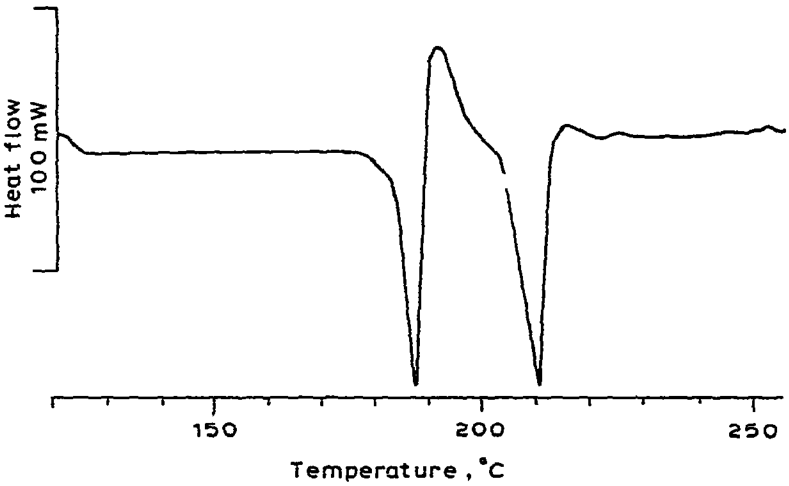


Fig 10. Partial DSC curve of compound (VII)

nitrogenation of (I)–(IV) can explain the existence of the above-mentioned intermediate products. The citraconimide olefins can polymerize under the experimental conditions, and their polymers, of course, have relatively higher thermal stabilities than the corresponding cyclopropane derivatives (VIII), (X), (XII) and (XIV).

Compound (XVII) melts at 181°C, as indicated by the endothermic peak on the DTA curve (Fig. 5), and confirmed by the Kofler hot bench test, whereas the equivocal decomposition product from compound (III) is already present in the molten state after the denitrogenation. This unexpected behaviour can be attributed to the presence of compound (XII) together with another compound of type (XIII) which greatly depresses the melting point. Above 285°C, the decomposition of (XVII) proceeds at an appreciable rate. The decomposition, however, is described by two DTA peaks, exothermic between 285 and 350°C and endothermic between 350 and 418°C. Above 420°C, the residue is composed of carbon. In the case of compound (XII), the decomposition becomes appreciable above 250°C, and the exothermic process occurs between 300 and 375°C, while the endothermic process occurs between 375 and 440°C. The residue undergoes slow decomposition above 440°C to end up with carbon at 535°C. It may be concluded, therefore, that the decomposition reaction is not simple and more than one product is formed. Some of the products can be stable hydrocarbons, the formation of which is accompanied by the liberation of heat.

The DTA curves of the 9-fluorene derivatives (IV) and (VII), showed two endothermic peaks in the same temperature range. The first refers to the melting, while the second is the isomerization. The slight difference in the melting temperatures indicates that the analyzed samples are of almost identical structure.

The purity of the compounds was tested on the basis of the broadness of the DSC peaks and consequently, the depression in the melting points [10] The melting points were, as measured, by DSC (Fig. 10), 180.4°C and 186.1°C, respectively, whereas the predicted values were 184.1°C and 187.4°C. The purity estimated on this basis was 95.21% and 98.65% for compounds (XIV) and (XVIII), respectively. Thus, one can conclude that the cyclopropane derivatives are the only products formed by the controlled pyrolysis of compounds (IV) and (VII), which reflects the action of the fluorene ring on the thermodynamic and thermal stability of the cyclopropane ring. These primary decomposition products show, as indicated by the second endothermic peak (Figs. 6 and 7), a pronounced tendency to isomerize to the more stable olefins (XV) and (XXI), where the gain in stability is due to an increased double conjugation. The isomerization is irreversible, because the cooling DTA curves of both compounds indicated only one exotherm, referring to the solidification of the melt. The solidification occurred far below the melting points quoted above, which ensures that a compound other than that melted is present (Figs. 6 and 7).

These products decompose above 305°C and 290°C in a multi-step reaction as indicated from the complication of the DTG curves (Figs. 6 and 7). Again, the decomposition starts exothermic and becomes endothermic when the extent of the decomposition is about 30%. The decomposition temperature intervals extend beyond 500°C.

Further studies are in progress to investigate the thermal behaviour of pyrazolinoisoimides and the dependence of the decomposition routes on the stereochemistry, to gain more insight into the decomposition mechanism.

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