



Flash vacuum pyrolysis of azolyacroleins and azolybutadienes

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ARTICLE INFO

Article history:

Received 7 July 2011

Received in revised form 26 October 2011

Accepted 14 November 2011

Available online 26 November 2011

Keywords:

Pyrolysis

Tetrazole

Nitrilimine

Indazole

Nitrogen extrusion

ABSTRACT

2-Aryl-5-acroleinyl-1,2,3,4-tetrazoles (**1a–d**) and 2-aryl-5-butadienyl-1,2,3,4-tetrazoles (**1e–g**) were subjected to flash vacuum pyrolysis. Acroleinyl derivatives resulted in nitrogen extrusion to give nitrilimines followed by ring closure to give the corresponding indazoles **3a–d** in good yields. On the other hand, butadiene derivatives underwent ring fragmentation to give *p*-substituted anilines without formation of the expected indazoles. Differences between thermal behaviour of 2-(4-chlorophenyl)-5-acroleinyl-1,2,3,4-tetrazole (**1c**) and 1-(4-chlorophenyl)-4-acroleinyl-1,2,3-triazole (**2**) were studied in details. DFT calculations have been used to examine the nitrilimine and carbene nature of the intermediates involved in the thermal reactions of azoly derivatives.

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1. Introduction

Flash vacuum pyrolysis (FVP) consists of subjecting a molecule to high temperature over a short period of time ($\sim 10^{-2}$ s). This process allows the acquisition of kinetic as well as unstable products and may be suitable for synthetic purposes or for the study of reaction mechanisms. FVP is used both as a single-step synthetic procedure and as a complement to a multistep synthesis. These reactions are generally clean and without solvent, so allow exploration of reactive species, such as carbenes, radicals, nitrenes and concerted reactions. Thus, FVP is an excellent technique for the study of intramolecular reactions, such as elimination, cyclization and generation of products that cannot be prepared in solution in thermal reactions. Several reviews concerning FVP have been reported¹ and a worldwide book concerning synthetic gas-phase transformations has also been published.² Many nitrogen heterocyclic compounds including pyrazoles, isoxazoles, triazines, triazoles and tetrazoles have been studied under thermal gas-phase conditions as an appropriate way to obtain new heterocycles.³

In the course of our pyrolytic studies we have focused on rings containing N–N double bonds, due to their ability to eliminate nitrogen, generating reactive species, which could undergo rearrangement to give monocyclic and fused *N*-heterocyclic compounds.

In particular, thermolysis of 1,5-disubstituted tetrazoles differs from that of the 2,5-disubstituted derivatives because nitrogen elimination in the former case produces nitrenes and carbodiiimides that rearrange to pyrazoles,⁴ thiadiazoles,⁵ oxadiazoles⁶ and triazoles⁷ while in the latter gives nitrilamines.⁸

In this work, FVP methodology has been applied to prepare new acroleinylindazoles (**3a–d**) in good yields starting from 2-aryl-5-acroleinyltetrazole precursors **1a–d**. In contrast to this result, 2-aryl-5-butadienyltetrazoles **1e–g** afforded *p*-substituted anilines rather than indazoles. In addition, FVP reactions of 1-(4-chlorophenyl)-4-acroleinyl-1,2,3-triazole **2** were performed in order to assess the reactivity of tetrazole and triazole rings under similar thermal conditions (Fig. 1). Theoretical calculations concerning the assumed nitrilimine and carbene intermediates were also performed to understand the mechanism operating in the nitrogen elimination of azoly derivatives **1** and **2**.

2. Results and discussion

Acroleinyltetrazoles (**1a–d**) and butadienyltetrazoles (**1e–g**) were prepared from 3-aryltetrazolo[1,5-*a*]pyridinium salts, whereas 1-(4-chlorophenyl)-4-acroleinyl-1,2,3-triazole (**2**) was prepared from 1,3-diaryl[1,2,3]triazolo[1,5-*a*]pyridinium salts according to a literature procedure.⁹ In all cases the trans isomers of **1** and **2** were used in the thermal reactions. FVP reactions of these azoly derivatives were performed in a Vycor glass reactor with

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¹ Deceased.

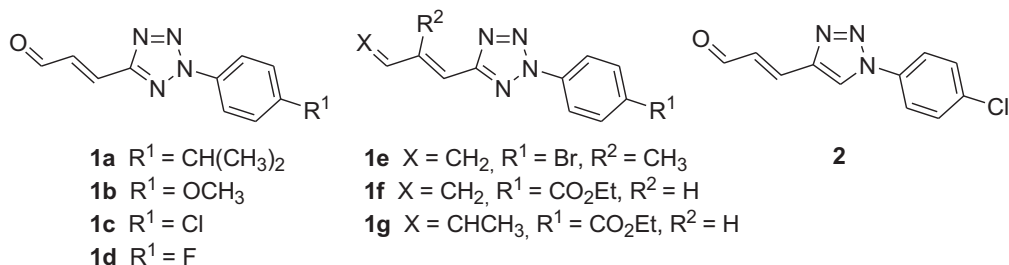


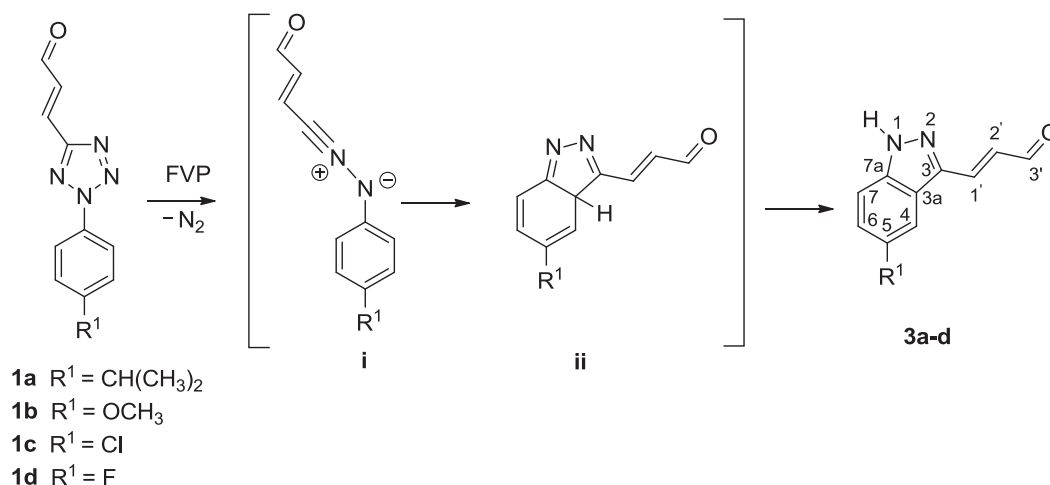
Fig. 1. Azolyl derivatives studied under FVP conditions.

pressures of $\sim 10^{-2}$ Torr and contact times of $\sim 10^{-2}$ s. In the case of substrate **1g** all efforts to achieve volatilization of the sample failed, and the low vapour pressure of this compound promoted decomposition in the sample probe without passage through the hot tube.

Gas-phase reactions of acroleinyltetrazoles (**1a–d**) were carried out between 250 and 370 °C (Scheme 1). These reactions were clean and 3-acroleinylindazoles (**3a–d**) were obtained in high yields (60–98%). The results are summarized in Table 1. In all cases, when a 100% conversion of the starting tetrazole was achieved, small amounts of two by-products: formylindenes **4** and indenenes **5** were also detected (Scheme 2).

isomerizes to the more stable aromatic tautomers 1*H*-indazoles **3a–d**.

This intermediate (**i**) is, however, a flexible molecule, which can adopt its geometry depending on the reaction conditions.^{8a,10} The generation of nitrilimines from 2,5-disubstituted tetrazoles has been previously studied in thermal^{8a,10} and photochemical reactions.¹¹ Thermal studies in the gas and solution phase have shown that 2,5-disubstituted tetrazoles are usually less stable than 1,5-disubstituted ones,¹² and that the intermediate nitrilimine reacts according to the temperature, solvent and nature of the substituent in position 2 of the initial tetrazole. Thus, electron-withdrawing substituents decrease the energy barrier of the



Scheme 1. Formation of 3-acroleinylindazole (**3**) by FVP starting from tetrazolylacrolein (**1**).

Table 1
FVP reactions of tetrazoles **1a–d**

Compound	R ¹	T (°C)	% 1	% 3 ^a	% 4+5
1a	CH(CH ₃) ₂	350	38	62	—
		370	—	92	8
1b	OCH ₃	250	55	28	17 (1:6) ^b
		280	5	60	35 (1:8)
		300	—	37	63 (1:12)
1c	Cl	250	39	61	—
		300	1	95	4
		250	27	73	—
1d	F	250	—	98	2

^a Values determined by ¹H NMR spectroscopy.

^b Total amount and relative ratio of indenenes **4** and **5** determined by GC/MS.

The formation of indazoles **3a–d** could be rationalized by a nitrogen extrusion reaction in the starting tetrazole ring (Scheme 1). The intermediate proposed for these transformations is represented by the nitrilimine resonance structure (**i**), which initially undergoes a [1,5] dipolar cyclization with participation of one double bond of the phenyl ring to give 4*H*-indazoles (**ii**), which

transformation of tetrazole into the nitrilimine intermediate. We also observed that the fluoroaryl derivative **1d** was completely transformed into **3d** at a reaction temperature lower than that used with the other substrates.

When the temperature is high enough, 3*H*-indazole (**ii**), i.e., the precursor of **3**, eliminates nitrogen to give 1*H*-indene-carbaldehyde **4** via carbene intermediates **iii** (Scheme 2). In general, loss of this second nitrogen molecule in indazoles requires high temperature (800 °C) as reported in case of pyrolysis of 3-phenyl-indazole to give fluorene.^{10a} In our experiments, these reactions occurred at low temperatures (about 300 °C); therefore, thermal instability of indazoles **3a–d** could be ascribed to the electronic effect of an acroleinyl substituent. This behaviour resembles the transformation observed with nitrogen extrusion of 3-(2-furyl)-indazole, where benzofulvene derivatives were obtained at 400 °C.^{10b}

In all cases, compounds **4a–d** were detected as a mixtures of 5-substituted-1*H*-indene-1-carbaldehyde (**1H-5R1**) and 6-substituted-1*H*-indene-3-carbaldehyde (**1H-6R1**), which were in equilibrium. Thermal isomerization of indenenes is a well-known thermal reaction and the amount of each isomer depends on the reaction conditions.¹³

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