Flash Pyrolysis – Synthetic and Mechanistic Aspects*

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Abstract

Some examples of synthetically useful flash pyrolysis reactions are presented, and the reaction mechanisms are discussed. Cyanocyclopentadienes, -indenes, and -pyrroles are produced by pyrolysis of the appropriate triazoloarenes or isatins, or as the end products of carbene-nitrene rearrangements. Fulvenallene is formed from benzocyclopropene, phthalide, phenyldiazomethane, 7-norbornadienyl acetate, and other precursors. Cyclopropa [b]-naphthalene and cyclopropa [b]-1,6-methano [10]-annulene yield 2-ethynylindene and acenaphthene, respectively. α-Coumaranone yields fulvene. Pyrido- and pyrimido [2,1-a] isoindoles are obtained by carbene-carbene rearrangements, starting from v-triazolo [1,5-a]-azines. The pyrolysis of 5-aryltetrazoles leads to diazo-compounds, triazoloazines, or carbenes. 2,5-Diaryltetrazoles give indazoles or fluorenes, also obtainable from 2,4-diaryl-1,3,4-oxadiazolin-5-ones. Arylacetylenes, five- and six-membered hetaryl-acetylenes, isocyanamines, and ketenimines are formedby pyrolysis of appropriately 4-substituted isoxazol-5-ones.

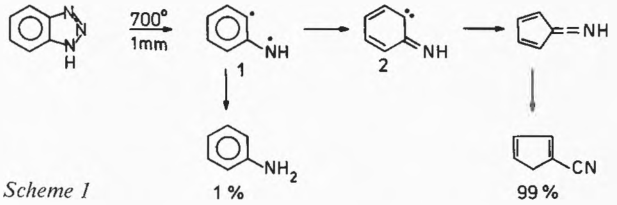
The technique of flash pyrolysis [1] involves the exposure of molecules to high temperatures for very short periods of time, e.g. between 10^{-3} and 10^{-1} seconds. For preparative purposes, this is conveniently carried out by distilling or subliming the substrate through an electrically heated quartz tube connected to a liquid nitrogen trap and a high vacuum line. The vacuum to be used depends very much upon the nature of the phenomenon under investigation. For example, many secondary reactions are due to the formation of chemically activated ("hot") molecules, which rearrange or decompose prior to trapping. This can often be avoided by increasing the pressure to about 1 mm with the aid of nitrogen as a carrier gas.

Because the molecules experience relatively few collisions, the temperatures used in flash pyrolysis are, of necessity, much higher than those customarily used in organic chemistry. Hence the occasional contention that flash pyrolysis conditions are extremely violent ones***. That this is not the case is shown by the fact that an attempted distillation of phenyl azide at atmospheric pressure results in an explosion; however, the azide is recovered largely unchanged after "pyrolysis" at 300° and 10^{-2} mm. At lower pressure the azide can still be recovered at higher temperatures. Aryldiazomethanes can even be prepared at 400° in the gas-phase (see Scheme 15), although they decompose slowly in solution at room temperature.

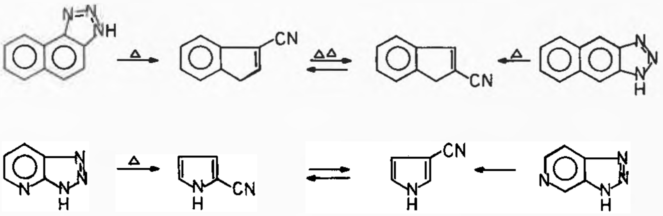
Flash pyrolysis is particularly useful for the isolation of kinetically unstable compounds which are often inaccessible by wet methods. In the following some examples, mainly from my Lausanne research group, are given.

Cyanocyclopentadienes

The pyrolysis of benzotriazole at 700 °C and 1 mm of nitrogen as carrier gas results in a 99% yield of 1-cyanocyclopentadiene together with a 1% yield of aniline (Scheme 1). The latter can be rationalized as arising from hydrogen capture by a 1,3-diradical (**1**), an unfavourable process under the low pressure conditions. The 1-cyanocyclopentadiene is ascribed to a Wolff-type ring contraction in iminocyclohexadienylidene (**2**). In a similar manner, substitued benzotriazoles, naphthotriazoles, and 1*H*-triazolopyridines yield the corresponding cyanocyclopentadienes, cyanoindenes, and cyanopyrroles (Scheme 2) [2]. All these compounds are difficult to synthesize by other means.

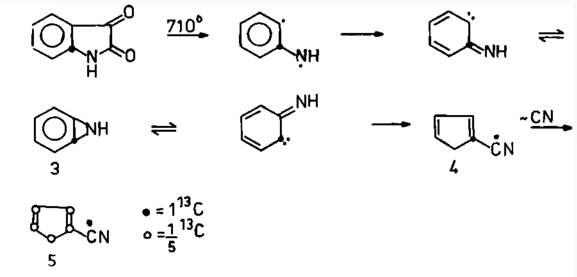


Scheme 1



Scheme 2

Cyanocyclopentadiene itself dimerises rapidly at room temperature, and the dimers cannot be completely monomerized. The five-ring nitriles undergo sigmatropic shifts of the cyano group at elevated temperatures, resulting in interconversion of the 2- and 3-cyanoindenes and the 2- and 3-cyanopyrroles [2].



Scheme 3

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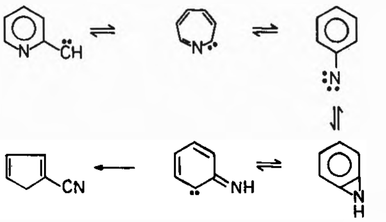
[***] One well known chemist has described it as hitting the molecule over the head with a sledge-hammer.

Cyanocyclopentadiene is also formed by the extrusion of two molecules of CO from isatin (Scheme 3). The mechanism of ring contraction was examined in this case by pyrolysis of 7a-^{13}C-isatin at 710°/10^{-3} mm. The observed CN/C_{ring} label ratio of 5:1 in the product (**5**) demonstrates the intermediacy of 1*H*-benzazirine (**3**) prior to ring contraction. The initial product **4** cannot be isolated due to the rapid shifts of the cyano group, which result in scrambling of the ring label over the five ring carbon atoms [3]. This mechanism is further supported by the fact that isatins substituted by methyl groups in the benzenoid ring yield small amounts of the two toluidines required by the 1*H*-benzazirine intermediate [4].

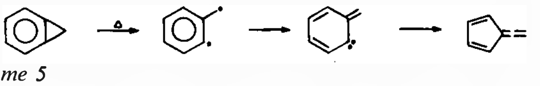
Furthermore, cyanocyclopentadiene is a rearrangement product of phenylnitrene (from phenyl azide) as well as of all the pyridylcarbenes in the gas-phase. ^{13}C-labelling and product studies have established that the pyridylcarbenes interconvert with phenylnitrene, and the labelling results strongly support the postulate that ring contraction takes place after isomerization of phenylnitrene to 1*H*-benzazirine (Scheme 4) [3].



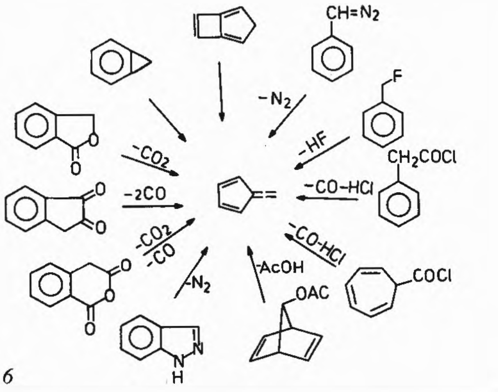
Scheme 4

Fulvenallene

The interconversion of 1*H*-benzazirine and iminocyclohexadienylidene has an all-carbon analogy in benzocyclopropene and methylenecyclohexadienylidene (Scheme 5). The Wolff-type rearrangement product of methylenecyclohexadienylidene, fulvenallene, is easily prepared by pyrolysis of benzocyclopropene [5], as well as from several other precursors shown in Scheme 6 [6].

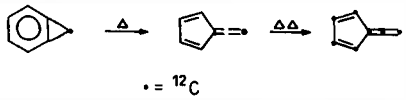


Scheme 5



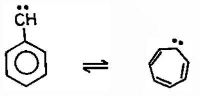
Scheme 6

The mechanism of ring cobtraction in benzocyclopropene was examined by pyrolysis of the 1-^{12}C-derivative (depleted of ^{13}C) (Scheme 7) [7]. While benzocyclopropene is a kinetically unstable molecule, it is stable up to 500° under flash pyrolysis conditions, and it can, indeed, be prepared by pyrolysis [8]. The rearrangement to fulvenallene is complete at ca 700° [5]. The pyrolysis of 1-^{12}C-benzocyclopropene at 750°–800° resulted in a largely specifically labelled fulvenallene which, when repyrolyzed at 1000°–1050° underwent complete automerization (Scheme 7).



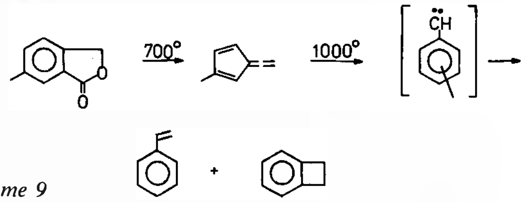
Scheme 7 • = ^{12}C

This astounding result can be understood if fulvenallene interconverts with phenylcarbene. The latter in turn is known [9] to interconvert with cycloheptatrienylidene (Scheme 8) and to undergo ring contraction to fulvenallene with complete carbon scrambling by flash pyrolysis [10]. If such a mechanism were operating, a methylfulvenallene should interconvert with a tolylcarbene (Scheme 9) which is known [11] to rearrange to styrene and benzocyclobutene by means of the ring expansion shown in Scheme 8.



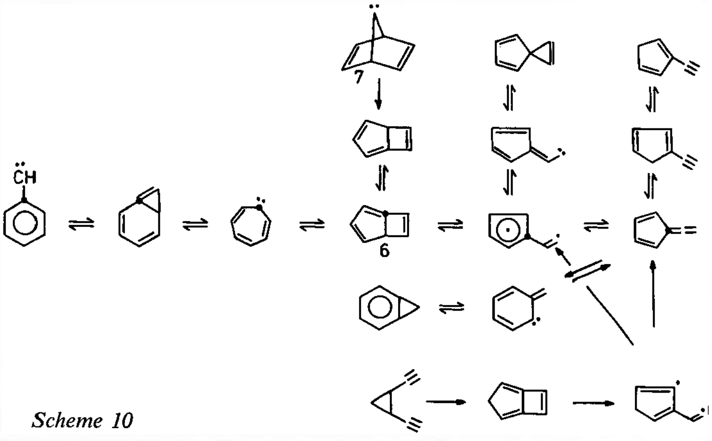
Scheme 8

Therefore, 2-methylfulvenallene was prepared by pyrolysis of 6-methylphthalide at 700°. Further pyrolysis of this fulvenallene at 1000° did in fact give a mixture of styrene and benzocyclobutene [12] (Scheme 9).



Scheme 9

So far, we have only shown that fulvenallene undergoes carbon scrambling, and that this probably takes place via phenylcarbene. We would like to know how the

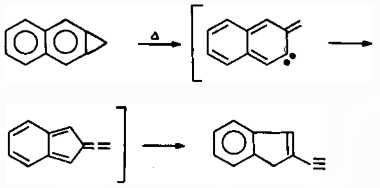


Scheme 10

carbon scrambling and ring contraction in phenylcarbene itself occur. On the basis of a new ^{13}C-labelling experiment on phenylcarbene we suggest that these complicated reations take place via bicyclo [3.2.0] hepta-1,3,6-triene (**6**) (Scheme 10). This seems to be the most rational way to explain the observation that 1-^{13}C-phenylcarbene at 590 °C/1 mm N_2 gave a fulvenallene with an excess of label at the 5-position.
Scheme 10 also shows several other known or postulated intermediates and routes to fulvenallene on the C_7H_6 energy surface. (For the diethynylcyclopropane route, see ref. [6f]; spiro[2.4]heptatriene and fulvenylcarbene [not yet reported to yield fulvenallene]: cf. ref. [13]; ethynylcyclopentadienes: ref. [5, 6a–b]; for the existence of cycloheptatetraene, a valcene isomer of cycloheptatrienylidene, see also ref. [14].) It is of particular interest that flash pyrolysis of 7-norbornadienyl acetate at 450° may yield 7-norbornadienylidene (**7**) [15] which rearranges to **6** and then to cycloheptatrienylidene and its dimerization product, heptafulvalene [16]. The pyrolysis of 7-norbornadienyl acetate at 800 °C resulted in the formation of fulvenallene [17]. The new mechanisms of ring contraction in phenylnitrene and phenylcarbene (Schemes 4 and 10) are quite different. To some extent the sames types of intermediates occur, but in a different order in the two schemes. In other words, the barrier hights separating the various intermediates must be different in the two systems.

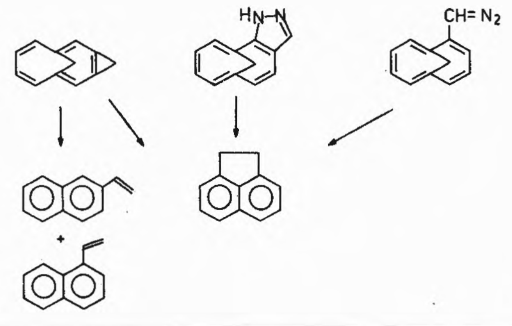
Pyrolysis of naphthalene and [10]annulene derivatives

The pyrolysis of cyclopropa[b]naphthalene yields 2-ethynylindene [18] (Scheme 11). Quite a different type



Scheme 11

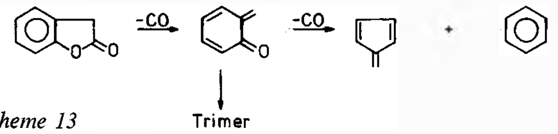
of product is found in the pyrolysis of the cyclopropa-, pyrazolo-, and diazomethyl-derivatives of 1,6-methano[10]annulene shown in Scheme 12, all of which yield acenaphthene as a major product at 500°–700 °C. Deuterium labelling of the central bridge in the cyclopropa [10] annulene resulted in scrambling of deuterium among all positions in the products. The compound labelled with ^{12}C in the lateral cyclopropene ring has been prepared, and the positions of label in the products are being determined [19].



Scheme 12

Fulvene

In contrast to phthalide, which yields fulvenallene after CO_2-elimination (Scheme 6), the isomeric α-coumaranone extrudes only CO by flash pyrolysis (Scheme 13).

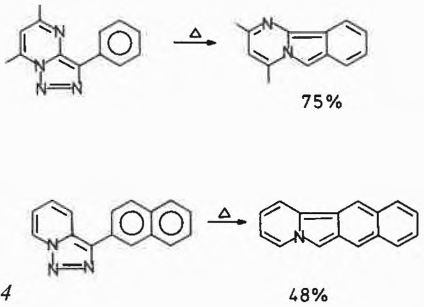


Scheme 13

The resulting intermediate either trimerises, or loses one more molecule of CO with formation of a solution of fulvene in benzene. Although the yield is low, this reaction represents a simple, one-step synthesis of fulvene [5].

Pyrido- and pyrimido[2,1-a]isoindoles

Condensed isoindoles (Scheme 14) are obtained from

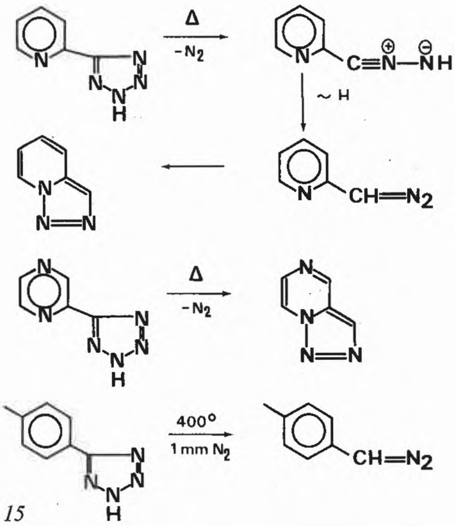


Scheme 14

triazoles by means of a series of carbene-carbene rearrangements of the type described in Scheme 8. Flash pyrolysis is the method of choice for the synthesis of isoindoles of this kind, since these compounds are highly reactive in solution. The pyrimido[2,1-a]isoindole system was previously unknown, and it is doubtful whether it could be prepared in solution at all. It is obtained as yellow crystals by pyrolysis of the triazolo [1,5-a] pyrimidine at 400 °C. Likewise, benzopyrido[2,1-a]isoindole is obtained as dark red crystals (Scheme 14) (while the positions of benzo-annelation have not been determined, the linear structure shown is the most likely). In a similar manner, fluorenes, azafluorenes, and carbazoles can be prepared in high yields by pyrolysis of diaryldiazomethanes or 3-aryl-v-triazolo[1,5-a]pyridines [20].

Triazoles and diazo-compounds from tetrazoles

The pyrolysis of 5-aryltetrazoles has proven to be a most convenient way to produce arylcarbenes in the gas-phase. The tetrazoles first eliminate one molecule of N_2 to give an intermediate which may be a nitrile imine (Scheme 15). This intermediate rearranges to a

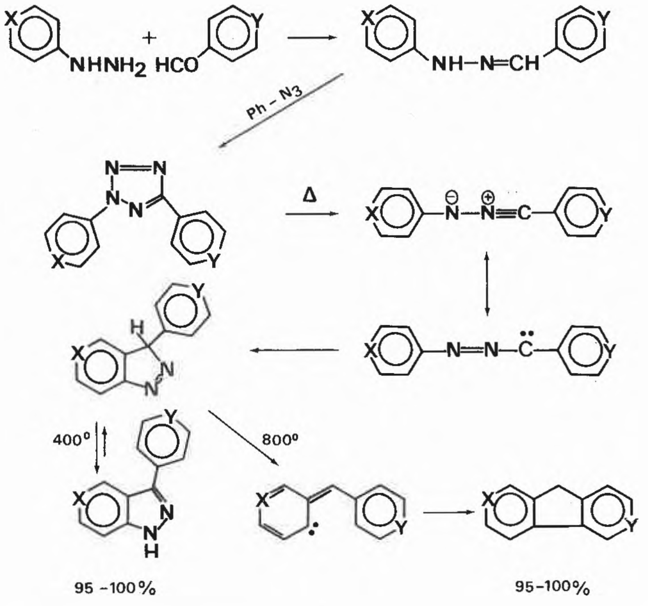


Scheme 15

diazo-compound, isolable as such from the pyrolysis of 5-p-tolyltetrazole. The 2-diazomethylpyridine cyclizes to v-triazolo[1,5-a]pyridine, which is isolable from the pyrolysis of 5-(2-pyridyl)tetrazole. v-Triazolo[1,5-a] pyrazine and v-triazolo[1,5-c] quinazolines, novel heterocyclic systems with purine-like skeletons, are similarly prepared by pyrolysis of 5-(2-pyrazinyl)tetrazole and 5-(4-quinazolyl)-tetrazoles, respectively. When these pyrolyses are carried out at higher temperatures, a second molecule of N_2 is lost, yielding the corresponding arylcarbenes [21].

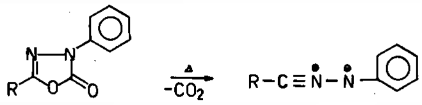
Indazoles and fluorenes from nitrile imines

By extrapolation from Scheme 15, 2,5-diaryltetrazoles are expected to yield disubstituted nitrile imines (Scheme 16). This reaction is known to occur in solution, where the nitrile imines can be intercepted in 1,3-dipolar cycloaddition reactions [22]. In the gas-phase at 400 °C, however, the nitrile imines undergo an electrophilic substitution onto the aromatic rings; the reaction can be formulated as taking place via the carbene resonance structure of the nitrile imine. The resulting indazoles are obtained in very high yields (Scheme 16) [23]. The same reaction can be observed even by pyrolysis of the diaryltetrazoles in inert solvents [24]. When the gas-phase reaction is carried out at 800 °C, a second molecule of N_2 is extruded, and the resulting diradical or carbene cyclizes to fluorenes or azafluorenes in near-quantitative yield (Scheme 16). For example, the highly unstable and otherwise difficultly accessible 3-azafluorene can be prepared in this way.



Scheme 16 X , Y = CR, N

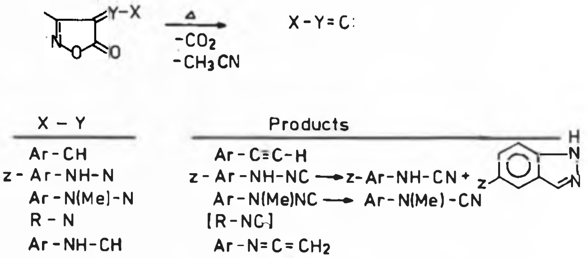
The nitrile imines can be produced also by gas-phase pyrolysis of 2,4-disubstituted 1,3,4-oxadiazolin-5-ones (Scheme 17; R = alkyl or aryl) [25].



Scheme 17

Acetylenes, isocyanamines, ketenimines, etc from isoxazolones

Another series of reactive intermediates, the methylidenecarbenes, can be generated by flash pyrolysis of isoxazolone derivatives (Scheme 18). Thus, 3-methyl-4-arylmethylideneisoxazol-5-ones (X-Y = ArCH) decompose into acetonitrile, carbon dioxide, and arylmethylidenecarbenes, the latter rearranging to arylacetylenes [26]. Heteroaromatic acetylenes, e.g. of the pyrrole, furan, thiophene, and pyridine series can be prepared similarly. The corresponding 4-arylhydrazones (X-Y = ArNH-N) give rise to intermediate isocyanamines which rearrange to either cyanamines or indazoles [27]. The imines (X-Y = R-N) may be expected to yield isonitriles [28]. The phenylaminomethylene-isoxazolone (X-Y = C_6H_5NH-CH) gave N-phenylketenimine [29]. Hopefully, it will also be possible to generate the fulminates, or O-esters of fulminic acid (R-O-NC) by pyrolysis of O-alkyl- or O-aryloximinoisoxazolones. While mercury and silver fulminates have been known since alchemical times [30], no organic fulminate has yet been prepared.



X − Y	Products
Ar-CH	Ar-C≡C-H
z-Ar-NH-N	z-Ar-NH-NC → z-Ar-NH-CN +
Ar-N(Me)-N	Ar-N(Me)NC → Ar-N(Me)-CN
R-N	[R-NC]
Ar-NH-CH	Ar-N=C=CH₂
Ar-O-N	[Ar-O-N≡C]

Scheme 18

Outlook

Flash pyrolysis can be used for the synthesis of many other interesting compounds or intermediates [1]. The procedure can be upscaled without difficulty and should find interest in the chemical industry, not least because reactive molecules can be obtained in high yields without any use of solvents. Although the reaction mechanisms may be of almost forbidding complexity (e.g. Scheme 11) good products are nevertheless obtained, and there is no reason to doubt that new and strange reactions will continue to be discovered.

Acknowledgements

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