Formation of Cumulenes, Triple-Bonded, and Related Compounds by Flash Vacuum Thermolysis of Five-Membered Heterocycles

Gloria I. Yranzo,[a] José Elguero,[b] Robert Flammang,[c] and Curt Wentrup*[d]

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Flash vacuum thermolysis of a large variety of heterocyclic compounds is a useful means of production of ketenes, ketenimines, thioketenes, allenes, iminopropadienones, bis(imino)propadienes, iminopropadienethiones, carbodiimides, isothiocyanates, acetylenes, fulminic acid, nitrile imines and nitrile ylides, nitriles, cyanamides, cyanates, and other compounds, often in preparatively useful yields.

Introduction

For many years, we have been involved in various aspects of flash vacuum thermolysis (FVT) for the purposes both of investigating reaction mechanisms and of synthesizing novel compounds on a preparatively useful scale. The coupling of FVT with matrix isolation, usually in Ar at ca. 10 K, and IR, UV, or ESR spectroscopy on one hand, and gas-phase mass spectrometry on the other has been particularly useful for the elucidation of structures of short-lived molecules.[1,2] Modern mass-spectrometric techniques, such as collisional activation (CA) and neutralization-reionization (NR) mass spectrometry have been directly applied to the species generated by FVT inside the ion source housing. Other researchers have used other techniques, such as photoelectron[3] and microwave spectroscopy, among others.[4] Preparative FVT has been reviewed elsewhere.[5]

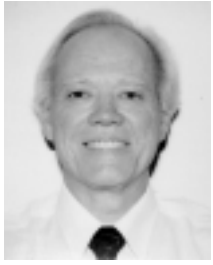
The purpose of this review is not by any means to give a comprehensive treatise on FVT reactions of 5-membered heterocycles, but rather to focus on reactions that are useful in producing novel types of molecules, in particular cumulenes and related compounds, that have been carried out in our own laboratories. It happens that many of these reactions have used 5-memebered heterocycles of various kinds as starting materials. This therefore serves to limit the size of this review.

[a] Instituto de Investigaciones Fisicoquímicas de Córdoba (INFIQC), Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria,
5000 Córdoba, Argentina
[b] Instituto de Química Médica, CSIC,
Juan de la Cierva 3, 28006 Madrid, Spain
[c] Laboratory of Organic Chemistry, Université de Mons,
7000 Mons, Belgium
[d] Department of Chemistry, The University of Queensland,
Brisbane, Qld. 4072, Australia
Fax: (internat.) + 61-7/3365-4580
E-mail: wentrup@chemistry.uq.edu.au

Gloria Inés Yranzo (top, left) was born in Rosario (Argentina) in 1957. She was educated in Córdoba (Argentina) and received her PhD in Organic Chemistry at the National University of Córdoba (Argentina) in 1983. During 1989 she joined Prof. Elguero's group in Madrid as a post-doctoral fellow and she is now Associate Professor in the Organic Chemistry Department, Faculty of Chemical Sciences of the National University of Córdoba. She is also a researcher of the National Research Council of Argentina (CONICET). Her research group is studying flash vacuum pyrolysis of heterocycles, mainly nitrogen heterocycles, and more recently she has included the use of heterogeneous catalysis in flash vacuum pyrolysis reactions.

José Elguero (top, right) was born in 1934 in Madrid, Spain. He studied chemistry at the University of Madrid (today Complutense) and then moved to Montpellier, France, where he received a PhD in 1961, working under the direction of Prof. Robert Jacquier. After more than twenty years in the French CNRS, he came back to Spain, to work at the Institute of Medicinal Chemistry (CSIC, Madrid). His research interests include, besides medicinal chemistry, heterocyclic, physical-organic and theoretical chemistry.

Robert Flammang (bottom, left) was born in Belgium and obtained his Docteur en Sciences Chimiques at the Université Libre de Bruxelles in 1970. In 1971 he joined the Université de Mons-Hainaut, where he is currently professor of chemistry and director of the Centre de Spectrométrie de Masse des Molécules (Bio)organiques. His research interests lie in mass spectrometry of organic molecules with the aid of tandem spectroscopic techniques such as collisional activation, neutralization-reionization, and ion-molecule reactions.



Curt Wentrup (bottom, right) was born in Denmark and studied chemistry at Københavns Universitet (Cand. Scient. with Prof. K. A. Jensen 1966; Dr. Scient. 1977) and the Australian National University, Canberra (PhD 1969). He was research assistant and privat-docent at the Université de Lausanne (Prof. H. Dahn) 1969–1976, professor at the Universität Marburg until 1985, moved to the chair of organic chemistry at The University of Queensland in 1985, and was elected Fellow of the Australian Academy of Science in 2000. His interests include reactive intermediates, unusual molecules, new functional groups, flash vacuum thermolysis, matrix isolation spectroscopy, and new synthetic methods based on the above.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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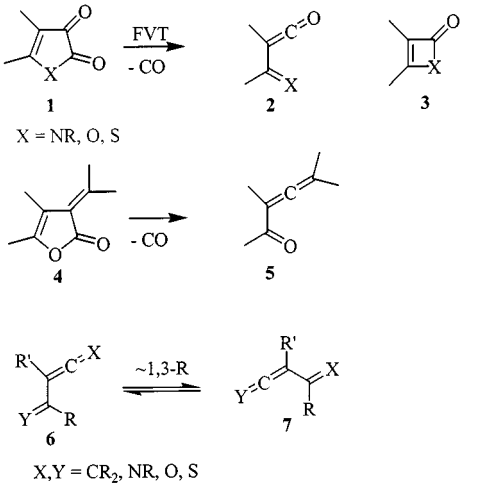
1. Acylcumulenes from Furans, Thiophenes, and Pyrroles

The cheletropic extrusion of CO from 2,3-dihydrofuran-2,3-diones, thiophene-2,3-diones, and pyrrole-2,3-diones **1** is a convenient method of generation of acylketenes, thioacylketenes, and imidoylketenes **2**.[6−8] This reaction can be applied in solution for preparative purposes,[9] and in the FVT mode for the direct investigation of the cumulenes. The 3-methylenefuran-2-ones **4** similarly afford acylallenes **5** (Scheme 1).[10] The thioacylketenes **2** (X = S) exist in equilibrium with the more stable (lower energy) four-membered ring thiolactones, thiet-2-ones **3** (X = S).[6] These latter are sensitive compounds, but are isolable in some cases, such as that of the naphthothietones (see below). The corresponding azetinones **3** (X = NR) are usually unstable with respect to the imidoylketenes **2**, but in certain cases they can be observed using matrix isolation techniques.[11]



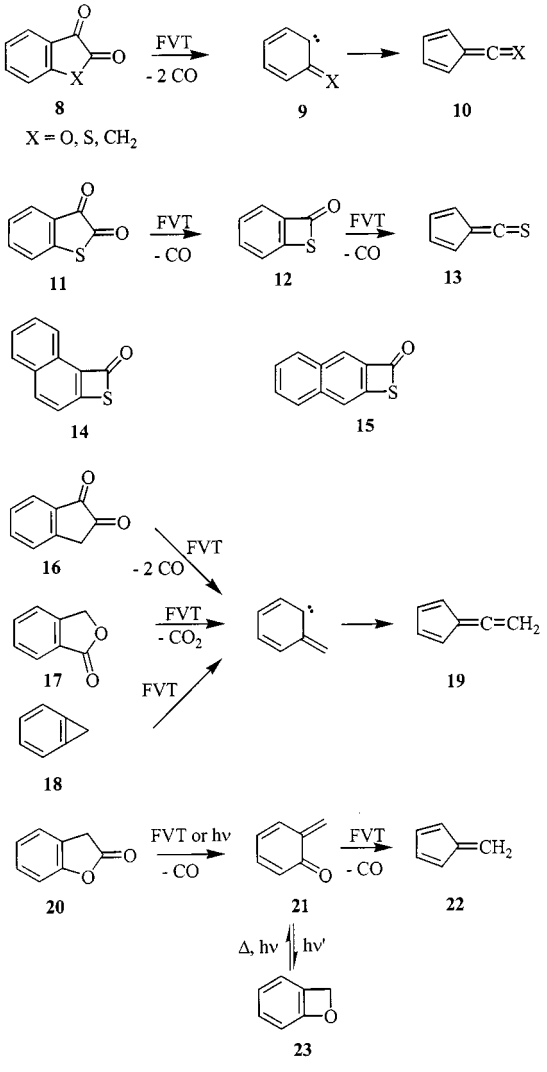
Scheme 1

An interesting property of the acylcumulenes **2** and **5** is their isomerization due to 1,3-shifts of the acyl substituents.[6] Thus, the acylketenes undergo degenerate rearrangements,[12] imidoylketenes interconvert with acylketenimines,[13] thioacylketenes with acylthioketenes,[14] and acylallenes with vinylketenes[15] (**6** → **7**). These rearrangements are facilitated by the interaction between a high-lying filled orbital (lone pair) on the migrating group R and a low-lying LUMO of the cumulene, which possesses a large in-plane coefficient on the central carbon atom.[16,17] The migratory aptitudes therefore follow the sequence H < aryl < RO < RS < R_2N. It has been demonstrated that these migrations of dimethylamino groups and of chlorine take place in solution at or below room temperature.[18,19]

2. Fulvenes and Cyanocyclopentadienes

The annelated heterocycles **8** afford heteroalkylidenecyclopentadienes **10**, presumably through cyclohexadienylidenes **9**.[9] The thiophene derivatives **11** afford thietones **12**, which in the naphtho-annulated cases (**14** and **15**), are stable, crystalline materials at room temperature.[20] Further FVT of thietones causes extrusion of CO and formation of thioketenes, such as the fulvene derivative **13**.[14,21]

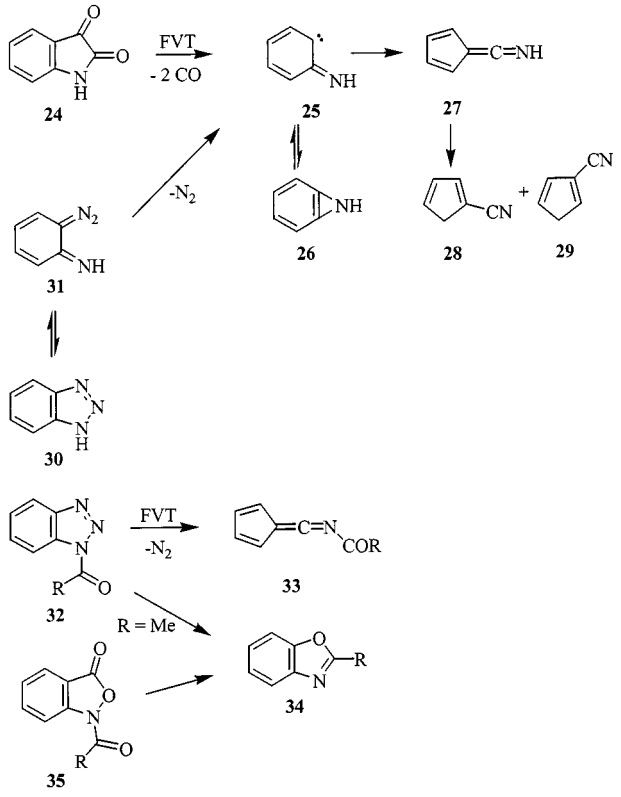
FVT of indandione **16**, phthalide **17**, and benzocyclopropene **18** have been used in a similar manner in the preparation of vinylidenecyclopentadiene ("fulvenallene" **19**) (Scheme 2).[22] Another isomer of phthalide, 2-coumaranone **20**, gives fulvene **22** instead, by double CO extrusion. This is a simple method for the production of dilute solutions of fulvene in benzene.[22c] *o*-Quinone methide **21** is generated from **20** both photochemically[23] and thermally,[24] and it can exist in photochemical equilibrium with benzoxete **23**. The latter can be stabilized by simple methyl substitution in the aromatic ring, but undergo thermal ring opening to **21**.[24]



Scheme 2

The benzannuleted pyrroledione isatin (**24**) should then logically be a precursor of the ketenimine **27** (Scheme 3). This, however, is an unstable compound, which tautomerizes to cyanocyclopentadiene (mainly the 1-isomer **28**,

accompanied by a little of the 2-isomer **29**). Cyanocyclopentadiene is short-lived at room temperature, dimerizing to a mixture of dimers, which can be dedimerized by distillation or gas chromatography. Use of ^{13}C-labelled isatin resulted in scrambling of the label between the CN group and the ring, thus demonstrating interconversion of **25** and benzazirine **26** prior to ring contraction to **28/29**.[25] All the ring carbon atoms in **28/29** become equivalent, due to rapid 1,5-sigmatropic shifts of H and CN around the cyclopentadiene ring under the FVT conditions. By using high vacuum conditions, it is possible to minimize the yield of aniline, formed through hydrogen abstraction.[26]



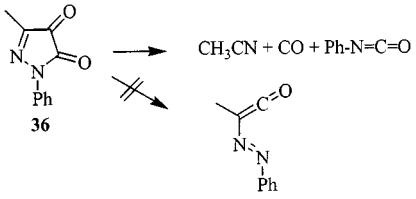
Scheme 3

Benzotriazole (**30**) is another excellent precursor of cyanocyclopentadiene **28/29**, which is formed in virtually quantitative yield.[27] The same intermediates, **25** and **27**, are presumably involved. These two intermediates, together with the diazo compound **31**, have been implicated in the matrix photolysis of **30**.[28] 1*H*-1,2,3-Triazolopyridines likewise afford cyanopyrroles.[27]

While detection of the ketenimine **27** in FVT reactions has not been achieved, it has been accomplished by IR and mass spectrometry in the FVT of the acetyl and benzoyl derivatives at 500−600 °C (**32** → **33**).[29] At higher temperatures, decomposition and rearrangement products are formed from the acetyl derivative; they include ketene, cyanocyclopentadiene **28/29,** methylcyanocyclopentadiene, benzonitrile, and 2-methylbenzoxazole (**34**) (up to 24% yield).[29] The latter compound is also obtained in over 90% yield by FVT of the benzisoxazole **35**.[30] There was no mention of ring-contraction products in this work. The formation of benzoxazole is analogous to the formation of furans from 1-acylpyrazoles, described in Section 4. Other aspects of triazole chemistry are described in Sections 4, 6, and 8.

3. Diazo Compounds, Nitriles, and Related Compounds from Pyrazoles

The dihydropyrazoledione **36** (Scheme 4) does not react in a manner similar to that of the simpler heterocycles **1**; no ketene derivative was detectable. Instead, the relatively weak N−N bond breaks, and the molecule fragments to MeCN, CO, and phenyl isocyanate.[31]



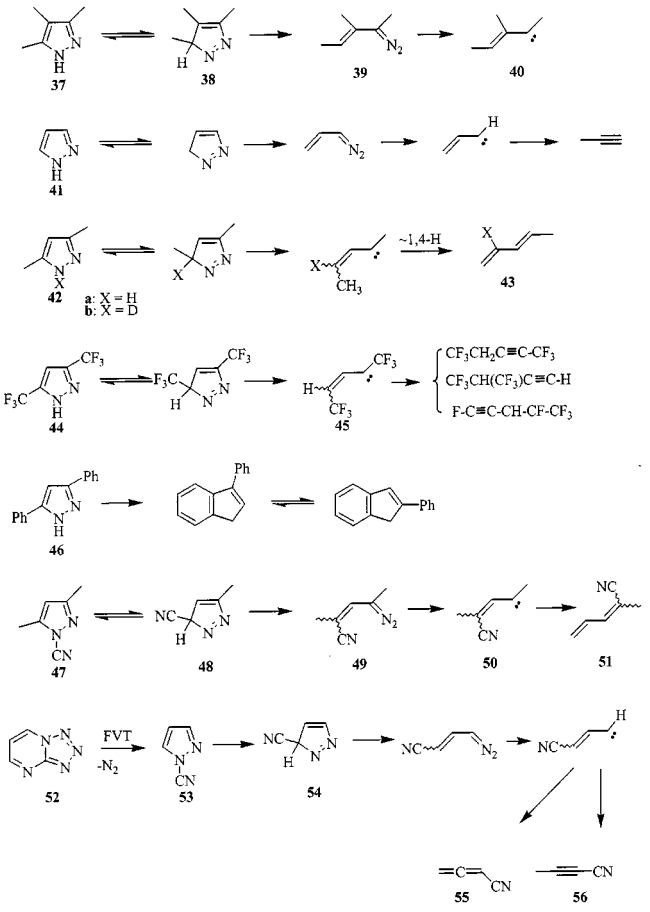
Scheme 4

When tautomerization or migration of the 1-substituents in 1,5-sigmatropic shifts is possible, pyrazoles **37** can isomerize to 3*H*-pyrazoles **38** as higher energy reactive intermediates. Ring opening of these produces vinyldiazomethanes **39**, which can eliminate nitrogen to generate vinylcarbenes **40** (Scheme 5). The overall activation barrier for this stepwise process is high, ca. 71 kcal/mol in the case of pyrazole **41**, and 67 kcal/mol for 3,5-dimethylpyrazole **42a** (log A = 15.4 and 15.1 s^{-1}, respectively).[32] This barrier is lowered to 60 kcal/mol in 3,5-bis(trifluoromethyl)pyrazole (**44**),[33] and to ca. 50 kcal/mol in 3,5-diphenylpyrazole (**46**).[34] The reaction product from pyrazole **41** itself is methylacetylene, while from 3,5-dimethylpyrazole (**42a**) it is 1,3-pentadiene. It has been shown by deuteration (**42b**) that the label appears exclusively in the 2-position in **43**; thus implying a 1,4-shift of H(D).[35]

Some useful fluorinated alkynes and dienes have been obtained in FVT reactions of 3,5-bis(trifluoromethyl)pyrazole (**44**) and 3(5)-methyl-5(3)-trifluoromethylpyrazole, through vinylcarbene intermediates such as **45**.[34]

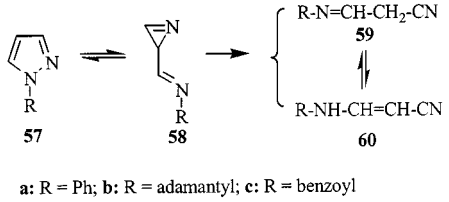
Cyano and methyl groups undergo 1,5-sigmatropic shifts on FVT of 1-substituted pyrazoles.[36] Thus, the 1-cyanodimethylpyrazole (**47**) affords 2-methylpentadienenitrile (**51**), presumably through the intermediates **48**−**50**. The simple 1-cyanopyrazole (**53**) is obtained by FVT of tetrazole **52** and reacts further to cyanoallene and tetrolonitrile **55** and **56**. 1,3,5-Trimethylpyrazole affords 2,3-dimethylbutadiene, 5-methylpentadiene, benzene, and dimethylpyrimidine, all in low yields.[36]

1-Substituted pyrazoles can undergo N−N bond cleavage in competition with the 1,5-sigmatropic shift described above. Thus, isomeric nitriles **59** and **60** have been obtained from 1-phenylpyrazole (**57a**),[37] 1-adamantylpyrazole (**57b**),[38] and 1-benzoylpyrazole (**57c**)[39] (for N_2 extrusion and recyclization to 2-phenylfuran see the following sec-



Scheme 5

tion). This reaction is thought to proceed through ring opening and isomerization to a 2*H*-azirine **58**, and further isomerization to the nitriles when no substituent is present at C-3 of the pyrazole ring (Scheme 6). A similar ring opening/azirine formation of isoxazoles is described in Section 9.[40] FVT of *N*-alkylpyrazoles with a β-hydrogen atom in the alkyl substituent affords alkenes in an elimination reaction involving a five-membered cyclic transition state.[41]



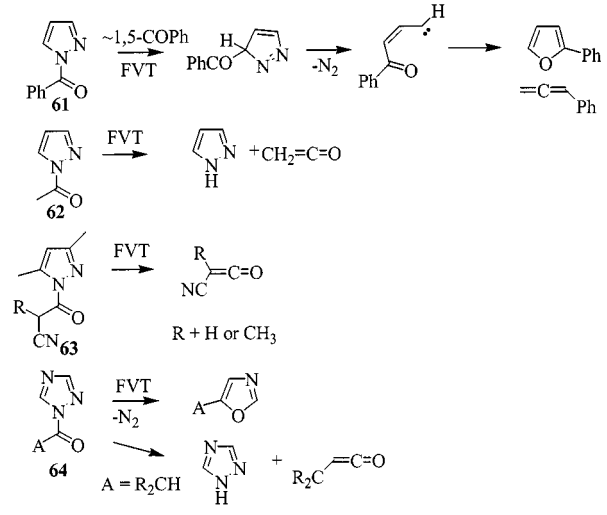
a: R = Ph; **b:** R = adamantyl; **c:** R = benzoyl

Scheme 6

Recently, FVT reactions over solid catalysts have been performed. This methodology opens new frontiers in FVT chemistry, as lower reaction temperatures may be used and different reaction pathways may obtain. The FVT of unsubstituted pyrazole over zeolites afforded methylacetylene, while treatment of 3,5-dimethylpyrazole (**42**) resulted in the formation of 1,3-pentadiene, 3-methylpyrazole, acetonitrile, and propionitrile through a [3+2] ring-fragmentation reaction. In contrast to the FVT reaction (Scheme 5), 3,5-diphenylpyrazole (**46**) did not give nitrogen extrusion products when pyrolyzed over zeolites, but the formation of 2,4(5)-diphenylimidazole was attributed to transition state selectivity in the zeolite cavity. 3,5-Diphenylpyrazole also afforded benzonitrile and phenylacetonitrile by [3+2] cycloreversion.[42,43] When hydrotalcytes were used in FVT reactions of 3,5-dimethylpyrazole **42** and 3,5-diphenylpyrazole **46**, only the nitriles arising from cycloreversion reactions were observed, showing pronounced selectivity for this reaction.[42]

4. Ketenes and Isothiocyanates from Azolides

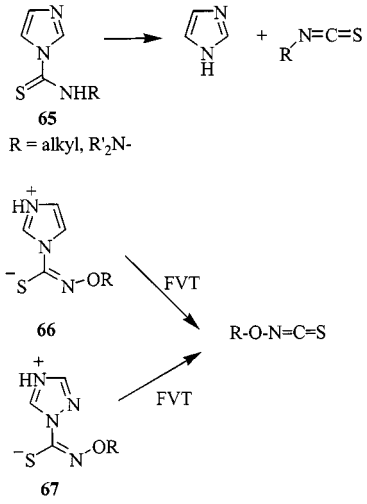
1-Benzoylpyrazole **61** (Scheme 7) undergoes a 1,5-sigmatropic shift of the benzoyl group, loss of N_2, and recyclization to 2-phenylfuran as the main product.[44,45] The formation of phenylallene and other minor products was also mentioned. The acetyl derivative **62** undergoes an elimination reaction, affording ketene and pyrazole almost exclusively.[44,46] This is a useful reaction, which has allowed the preparation of cyanoketenes (for example) by FVT of appropriately substituted acylpyrazoles **63**.[47,48] 1-Acyl-1,2,4-triazoles (**64**) react analogously, to give either ketenes by elimination or oxazoles through sigmatropic shift and N_2 loss.[49]



Scheme 7

In principle, pyrazolides and 1,2,4-triazolides can undergo intramolecular ketene formation of the types just mentioned. Imidazolides cannot, but they have the advantage of sometimes being less prone to hydrolysis than the pyrazolides, and FVT can still result in the desired products. This reaction has been used to generate isothiocyanates, RNCS, as well as dialkylamino isothiocyanates, $R_2N-N=C=S$, from imidazolides **65**[50] and as one of the methods of generation of the unstable alkoxy isothiocyanates, $R-O-N=C=S$, both from imidazolides **66** and from 1,2,4-triazolides **67** (Scheme 8).[51] The fact that these com-

pounds exist in the depicted zwitterionic forms probably facilitates the elimination reactions.

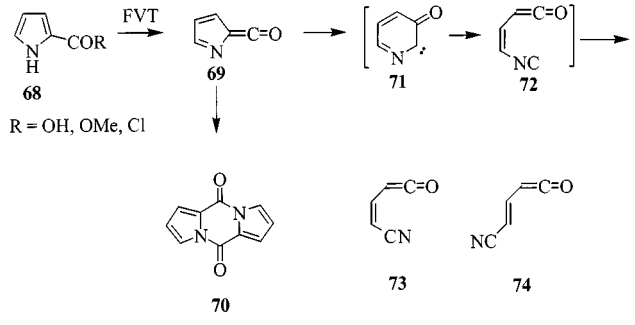


Scheme 8

5. Azafulvenones

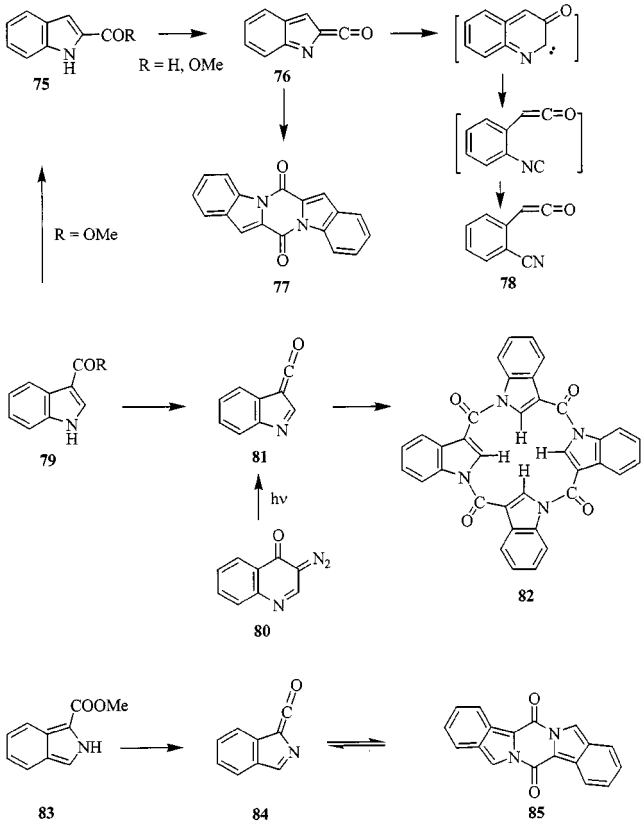
The pyrolysis of methyl esters is a well-known method of preparation of ketenes.[5] The carboxylic acids themselves or the acid chlorides may also sometimes be used. Ethyl esters usually eliminate ethylene to afford the carboxylic acids, which may either eliminate water to give ketenes, or decarboxylate.

The FVT of pyrrole-2-carboxylic acid, its methyl ester, or its acid chloride **68** generates the azafulvenone **69** (Scheme 9), which dimerizes to pyrocoll **70**. At higher temperatures, a mixture of nitriles **73** and **74** is formed, and a detailed investigation of the reaction mechanism indicates that, formally, a retro-Wolff rearrangement to carbene **71** and thence isonitrile **72** is involved.[52]



Scheme 9

The indole-2-carboxylic acid derivatives **75** similarly afford the diketopiperazide **77** and (*o*-cyanophenyl)ketene **78**. The 3-indole isomer **79** rearranges in large part to the 2-isomer **75**, and only a minor part affords the ketene **81**. This interesting ketene is obtained by matrix photolysis of diazo ketone **80** and, since it cannot dimerize to a diketopiperazide, it tetramerizes to the "*N*-confused" porphyrinogen analog **82** (Scheme 10). Isoindole **83** affords ketene **84**, which dimerizes to diketopiperazide **85.**[42]



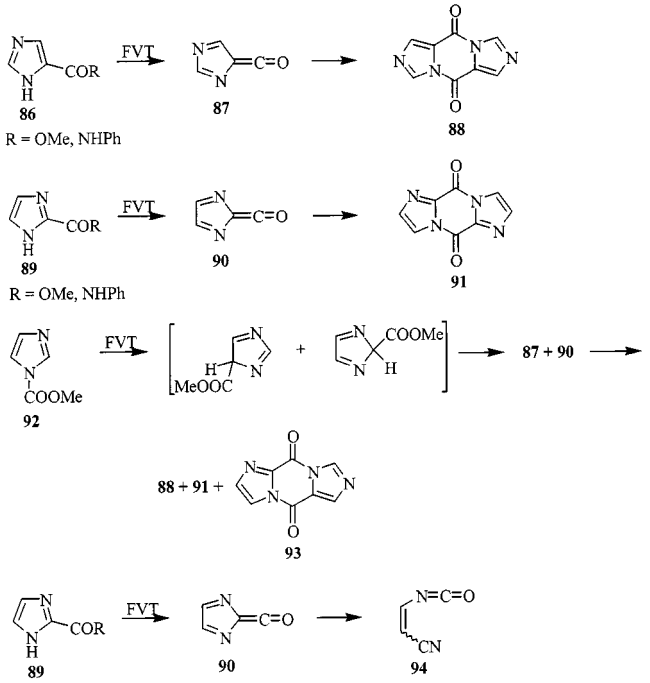
Scheme 10

The imidazole carboxylic esters and amides **86** and **89** give rise to azafulvenones **87** and **90**, respectively (Scheme 11).[53] These dimerize cleanly to diketopiperazides **88** and **91**, respectively. When 1-methoxycarbonylimidazole (**92**) is used, a sigmatropic shift converts it to a mixture of the 2- and 4-substituted isomers, from which a ca. 1:1 mixture of the two ketenes **87** and **90** is obtained. These therefore dimerize to a statistical mixture of piperazides **88**, **91**, and **93.**

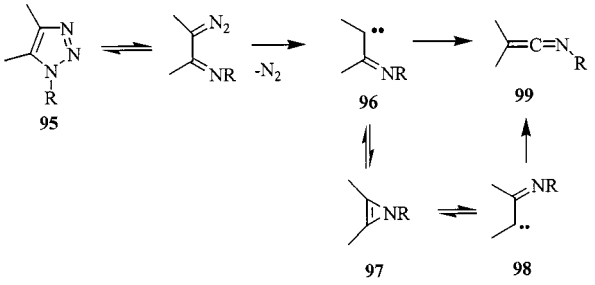
In this example too, further thermolysis causes ring opening in a retro-Wolff-type rearrangement to cyanovinyl isocyanate **94**, which was isolated in a cold trap (liquid nitrogen) and characterized by IR spectroscopy as well as by nucleophilic addition to the isocyanate function.[54]

6. Ketenimines from 1,2,3-Triazoles

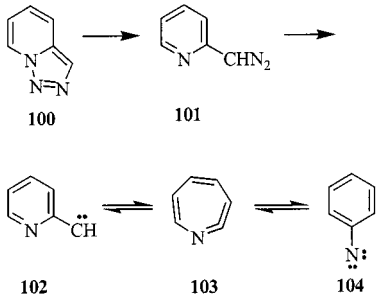
The chemistry of triazoles has been reviewed,[55] and the formation of fulvenes and cyanocyclopentadienes from benzotriazoles was mentioned in Section 2. Like 3*H*-pyrazoles (Section 3), 1,2,3-triazoles **95** can undergo ring opening to diazo compounds, nitrogen loss to imidoylcarbenes, and a Wolff-type rearrangement to ketenimines **99**, among other compounds. An example is the formation of *N*-cyanoketenimine.[56] The carbenes **96** and **98** can interconvert through 1*H*-azirines **97** (Scheme 12).[57]



Scheme 11



Scheme 12



Scheme 13

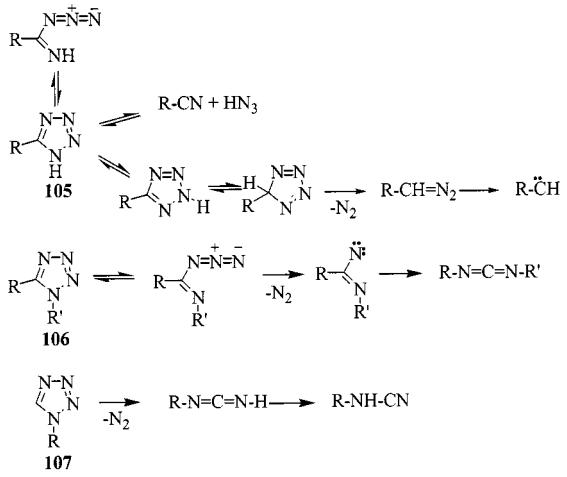
v-Triazolo[1,5-a]pyridines such as **100** (Scheme 13) are in equilibrium with the higher energy diazo isomers **101**.[58] Thermolysis (or photolysis) results in 2-pyridylcarbenes (**102**), ring expansion to 1-azacycloheptatetraenes (**103**), and interconversion with phenylnitrenes **104**. The nitrenes **104** are usually of lower energy than the valence-isomeric carbenes **102**, and so the final products are derived from the nitrenes (aniline, azobenzene, and cyanocyclopentadiene **28/29**).[59,60] The efficient synthesis of cyanocyclopentadiene from benzotriazole through a Wolff-type rearrangement was described in Section 2.

1-Methylbenzotriazole undergoes a 1,5-shift of the methyl group, interconverting it with 2-methylbenzotriazole, which is isolable at room temperature; the two isomers are separable by gas chromatography.[61] 1-Methylbenzotriazole also loses N_2 to produce *N*-phenylmethanimine,[30,61] which trimerizes. This trimer is also formed on FVT of 1-methylbenzisoxazole.[30] 1-Phenylbenzotriazole undergoes loss of N_2 and quantitative cyclization to carbazole.[62,63] 1-(2-Pyridyl)benzotriazole likewise affords pyrido[1,2-*a*]-benzimidazole.[30] Other aspects of triazole chemistry are described in Sections 2, 4, and 9.

7. Carbodiimides from Tetrazoles

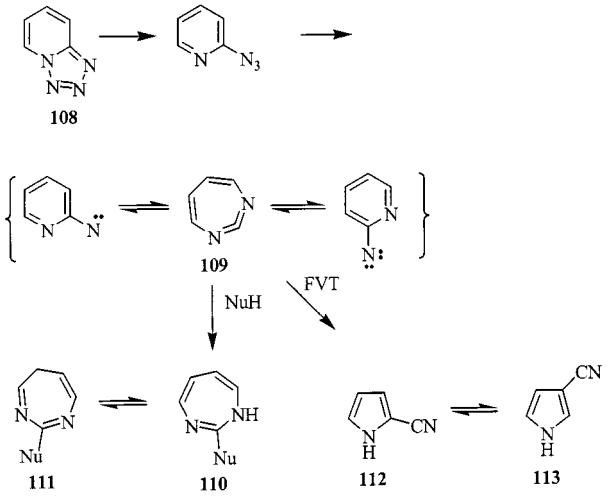
The chemistry of tetrazoles has been reviewed several times.[1,64–66] In principle, tetrazoles substituted in the 1- and/or 5-positions can exist in equilibrium with open-chain imidoyl azides. This is true for the monocyclic[67] and, in particular, bicyclic tetrazoles (such as tetrazolo[1,5-*a*]pyridines, tetrazolo[1,5-*a*]pyrimidines, tetrazolo[1,5-*c*]pyrimidines, etc).[64,66,68] The equilibrium constant is highly dependent on substituents, phase and solvents. Usually, electron-withdrawing substituents favor the azide forms, but exceptions are known.[69]

5-Substituted tetrazoles **105** can cleave in two ways: to nitriles and HN_3 (from which they are made), and to diazo compounds, which are precursors of arylcarbenes (Scheme 14).[58,70] 1,5-Disubstituted tetrazoles **106** are useful precursors of carbodiimides.[71] 1-Substituted tetrazoles **107** similarly give rise to monosubstituted carbodiimides, R−N=C=N−H, which can be isolated at liquid N_2 temperature but isomerize to cyanamides, RNH−CN, at ordinary temperatures.[72] 2,5-Disubstituted tetrazoles are precursors of nitrile imines, as described in the next section.



Scheme 14

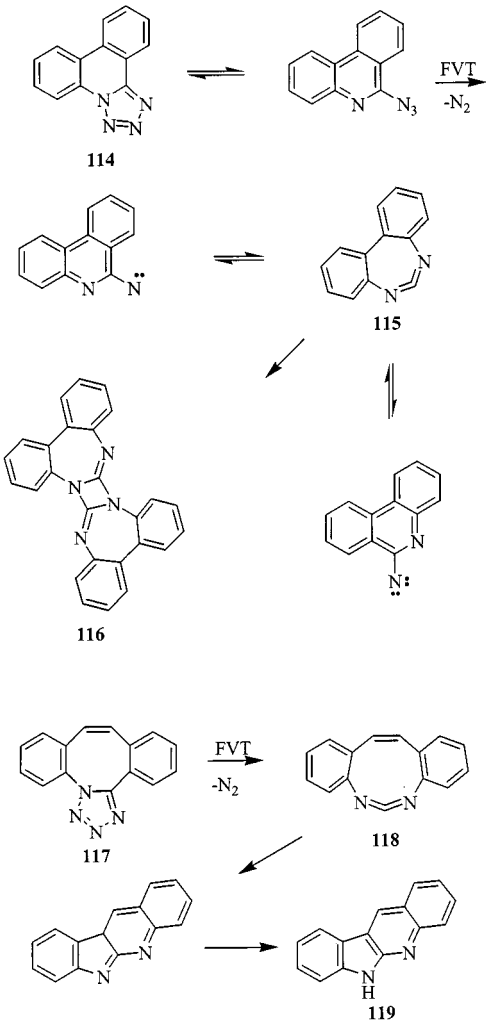
Tetrazoloazines (pyridines, pyrimidines, pyrazines, quinolines, isoquinolines, and phenanthridine) undergo ring opening to azides (often detectable by low-temperature IR spectroscopy after sublimation), N_2 elimination to nitrenes (triplets detectable by low-temperature matrix ESR and in some cases matrix IR spectroscopy), and ring expansion to cyclic carbodiimides (such as **108** → **109**). These reactions take place both on FVT and on photolysis. Solution photolysis allows the preparation of 1,3-diazepines **110** and/or **111** (Scheme 15). The final products of the gas-phase FVT reactions are cyanopyrroles **112** and **113** (2- and 3-cyanopyrroles interconvert under high temperature FVT conditions, due to sigmatropic shifts of H and CN). Smaller amounts of glutacononitrile (by ring opening), and 2-aminopyridine (by H-abstraction, probably from the triplet nitrene) are also formed.[59,60,73,74] The ring expansions (to 7-membered ring carbodiimides) and ring contractions (to 5-membered ring nitriles) and/or ring opening of several aza and benzo derivatives have been described.[59,60,66]



Scheme 15

The cyclic carbodiimide **115**, obtained from tetrazolophenanthridine **114**, is relatively long-lived, being easily isolable below −100 °C and dimerizing in high yield to the diazete derivative **116** at ca −45 °C; the structure of **114** has been proved by X-ray crystallography,[75] and it has been synthesized and analyzed a second time using a different type of precursor (Scheme 16)[76].

The 8-membered ring analog **117** yields the indoloquinoline **119** as the product.[77] Most probably, this reaction proceeds through transannular cyclization in the 9-membered cyclic carbodiimide **118**.[78] When the double bond in the 8-membered ring is hydrogenated, no such cyclization can take place, and ring contraction to *N*-cyano-10,11-dihydrodibenzo[*b*,*f*]azepine takes place instead.[78] The corresponding dibenzotetrazoloazonine also produces a transannular cyclization product, presumably through a 10-membered cyclic carbodiimide, whereas the dihydro analogue undergoes ring contraction to an *N*-cyanotetrahydrodibenzoazocine.[79]



Scheme 16

8. Nitrilium Betaines

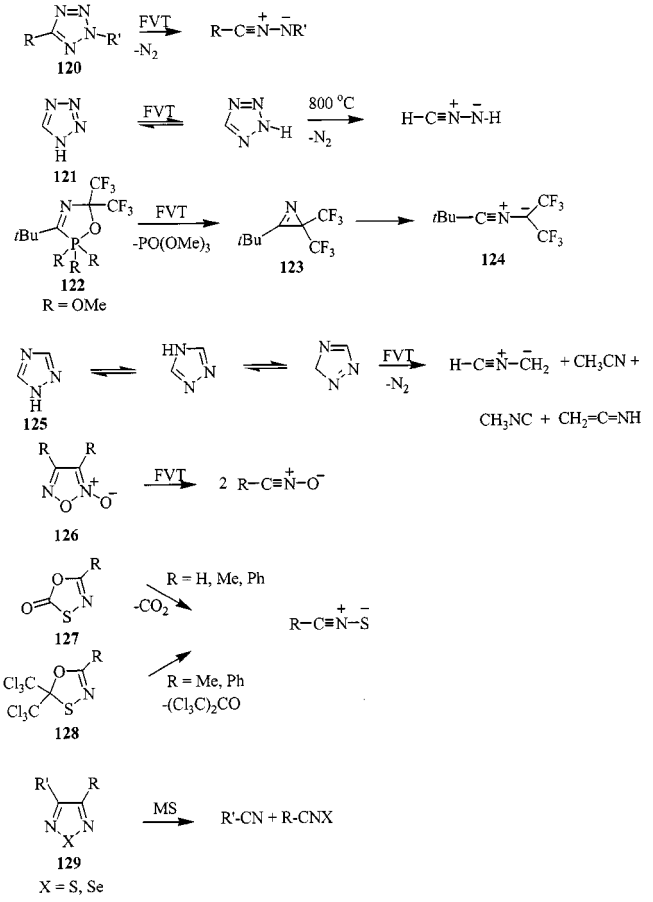
1,5-Disubstituted tetrazoles **120** are precursors of nitrile imines.[80,81] The unsubstituted nitrile imine, HCNNH, has been generated by FVT of tetrazole **121**, through tautomerization to the 2*H*-isomer.[82] X-ray crystal structures of several stable nitrile imines have been reported by the Bertrand group.[80] The structures can vary from nitrile-like (propargylic) to allenic, with a consequential wide range of frequencies in the main IR stretching vibration (2010−2230 cm^{-1}).[80]

There have been comparably few studies involving the direct observation of nitrile ylides, $RCNCR_2'$.[81] Direct observation of nitrile ylide **122** and azirine **123** by IR spectroscopy was possible upon FVT of oxazaphosphole **122**.[83] The unsubstituted formonitrile ylide, $HCNCH_2$, was obtained by FVT of 1,2,4-triazole **125**, which at high temperatures in the gas phase exists as a tautomeric mixture.[84] As in the case of nitrile imines, the structures of nitrile ylides are variable, but all give rise to strong IR absorptions in the range 1930−2320 cm^{-1}.[80]

Furoxanes **126** are FVT precursors of nitrile oxides, RCNO, from which they may be prepared by dimerization. The latter compounds include cyanogen oxide, NC−CNO, which has been investigated thoroughly in recent years.[85,86] Nitrile oxides may also be obtained by FVT of α-haloximes[87].

Oxathiazolones **127** generate nitrile sulfides, RCNS, with elimination of CO_2.[88,89] This method is useful for preparative cycloaddition chemistry of the transient nitrile sulfides, and FVT allows them to be observed directly, by low temperature IR spectroscopy or on-line mass spectrometry. The related heterocycles **128** also serve as precursors of nitrile sulfides.[64,65]

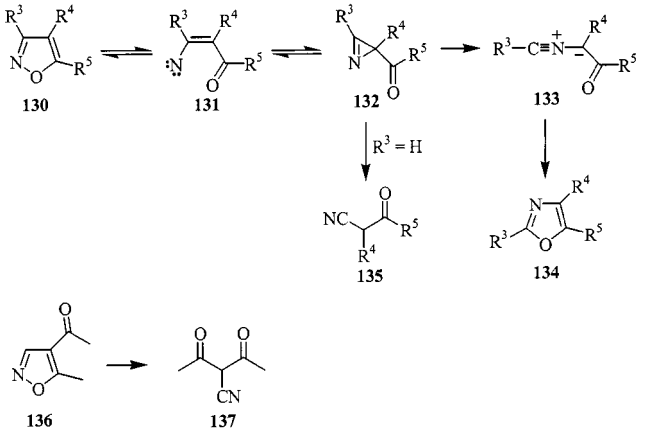
1,2,5-Thiadiazoles **129** (X = S; R = H, CN, NH_2, Cl; R′ = H, CN) generate nitriles and nitrile sulfides upon dissociative ionization in the mass spectrometer, but the yields of these compounds in FVT reactions are too low for unambiguous characterization by IR spectroscopy.[90] The selenadiazole **129** (X = Se; R = R′ = CN) similarly affords nitrile selenides, RCNSe, in the mass spectrometer (Scheme 17).[91]



Scheme 17

9. Azirines, Nitrile Ylides, and Nitriles from Isoxazoles

Isoxazoles **130** undergo cleavage of the weakest bond in the molecule, the N−O bond, like that of the N−N bond cleavage in pyrazoles (Section 3), to generate a putative vinylnitrene **131**.[66,92] The singlet nitrene may not actually be a minimum on the potential energy surface. 2*H*-Azirines **132** can in many cases be obtained as products of FVT (and/or photolysis) when there is a substituent R^3 at C-3 (R^5 = alkyl, OR, NR_2).[93] If R^3 = H, the final product is a nitrile, **135**, regardless of the nature of the substituent R^5 at C-5. For example, FVT of 4-acetyl-5-methylisoxazole (**136**) affords 3-cyano-2,4-pentanedione (**137**) (Scheme 18). The azirines **132** can also undergo ring opening to nitrile ylides **133** and recyclization to oxazoles **134** (R^3 = Me, Ph, NH_2);[94] this constitutes the frequently observed isoxazole-oxazole rearrangement (see also the following section). In the gas phase, 4-alkylideneisoxazol-5(4*H*)-ones are in tautomeric equilibrium with 4-alkenyl-5-hydroxyisoxazoles. The latter undergo ring opening to the vinylnitrenes and recyclization to pyrrole-3-carboxylic acids.[95]

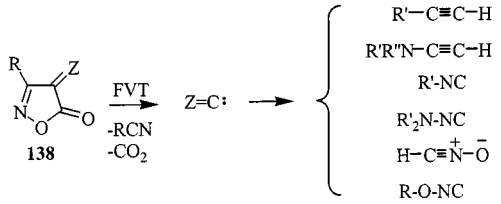


Scheme 18

10. Acetylenes, Isocyanides, and Cumulenes from Isoxazolones

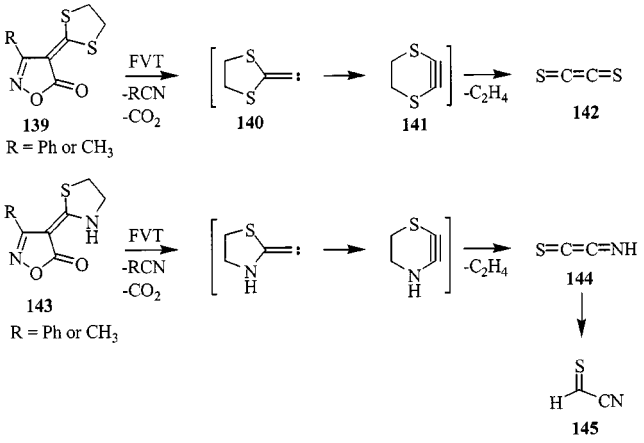
4-Substituted isoxazol-5(4*H*)-ones **138** are useful precursors for a variety of interesting compounds (Scheme 19). They usually decompose by initial breaking of the weak N−O bond, with consequent elimination of CO_2 and a nitrile R−CN, especially when R = CH_3. As we shall see below, aryl groups R can undergo 1,2-shifts that can produce other types of products. Thus, the 3-methylisoxazolones generate vinylidenes or isocyanides Z = C:, which afford acetylenes, aminoacetylenes (including those with primary and secondary amine functions), aryl isocyanides,[96] amino isocyanides, fulminic acid[97] (from the oxime **138**, Z = NOH), and fulminates, RONC (from **138**, Z = NOR).[98,99] This reaction constitutes a practical and high-yielding synthesis of many arylacetylenes and heteroarylacetylenes, some of which are not easily obtained in other ways.[100] The secondary aminoacetylenes easily tautomerize to ketenimines, and the primary ones to nitriles,[101,102] while the amino isocyanides rearrange to cyanamides.[103] The fulminates, RONC, isomerize to cyanates (R′ = Ph) or isocyanates (R′ = benzyl), or they fragment

to formaldehyde and HCN (R′ = Me) or to ethylene and fulminic acid (R′ = Et).[104]



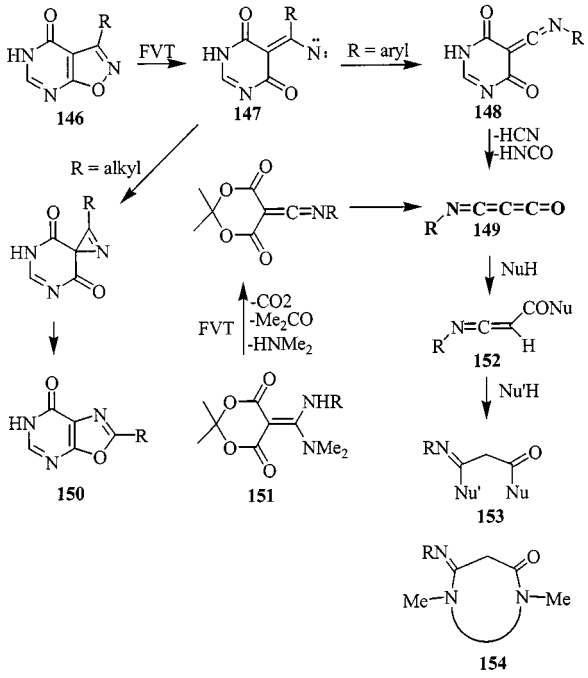
Scheme 19

Isoxazolones **139** have been used to generate the unstable ethenedithione S=C=C=S (**142**).[105] The reaction is thought to proceed through the vinylidene **140**, isomerization to the cyclic acetylene **141**, and fragmentation. Although ethenedithione polymerizes in the condensed state at ca. 60 K, it survives FVT generation at 1000 °C, and has been characterized by matrix IR and UV spectroscopy and mass spectrometry. It has also been generated from other precursors.[106] The imine analogue **144** has been generated analogously from **143** but isomerizes to thioformyl cyanide (**145**) under FVT conditions (Scheme 20).[107]



Scheme 20

Isoxazolopyrimidinones **146** were used by some of us in the first synthesis of iminopropadienones, R−N=C=C=C=O, **149**.[108−110] This reaction takes place when R is an aryl moiety capable of a 1,2-shift in the putative vinylnitrene **147**, resulting in the transient ketenimine **148**, which is detectable by on-line mass spectrometry. Compound **148** readily fragments to HCN, HNCO, and the iminopropadienones **149**. Alkyl groups are less prone to the 1,2-shift in the vinylnitrenes, and in their case the normal isoxazole-oxazole rearrangement takes place, to give oxazoles **150** as the final products.[111] The iminopropadienones **149** are also obtained by FVT of Meldrum's acid derivatives **151**, and this reaction is particularly useful preparatively.[108−110] Compounds **149** are isolable at liquid nitrogen temperature, and in some cases even at room temperature. They undergo synthetically interesting nucleophilic addition reactions at the C=O and C=N groups to afford ketenimines **152** as well as open-chain and cyclic malonic acid derivatives **153** and **154** (Scheme 21).



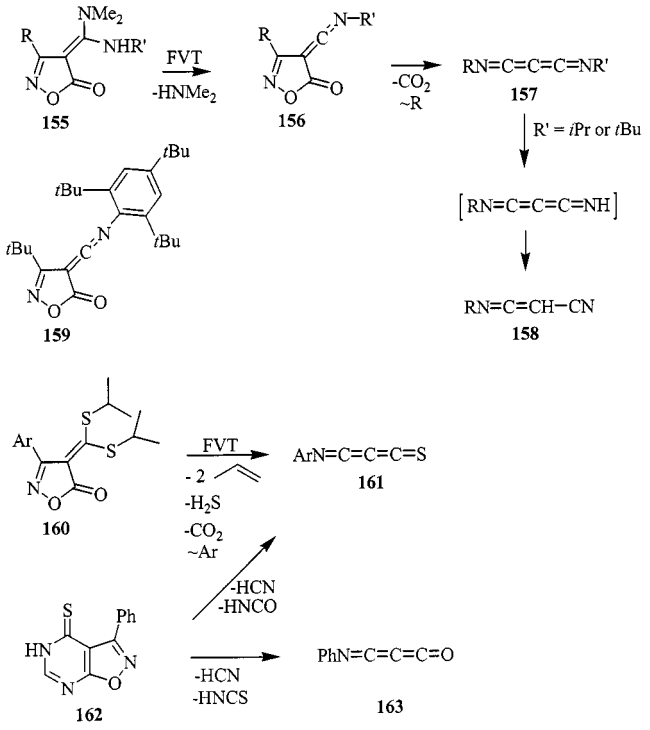
Scheme 21

Bis(imino)propadienes **157** are reactive intermediates, obtainable by FVT of bis(aminomethylene)isoxazolones of the type **155**.[112] Initial elimination of amine affords ketenimines **156**, which are sometimes isolable. The compound **159** is particularly interesting because the X-ray structure, as well as the unusual ^{13}C NMR and IR data, revealed that the Ar group is collinear with the C=C=N moiety.[112] Further studies demonstrate that ketenimines with two electron-withdrawing substituents (X) at the carbon atom tend to have such collinear $X_2C=C=N-R$ frameworks.[113] When either R or R′ can be eliminated as an alkene in the bis(imines) **157**, isomerization to cyanoketenimines **158** takes place.[112]

A similar sequence of eliminations produces aryliminopropadienethiones **161** from isoxazolones **160** (Scheme 22).[114] Compounds **161** are isolable at liquid nitrogen temperatures and undergo nucleophilic addition reactions with amines. By analogy with the use of **146** to produce iminopropadienones **149**, it might have been expected that isoxazolopyrimidinethiones **162** would also be precursors of iminopropadienethiones **161**. In fact, only small amounts of **161** are formed on FVT of **162**; the reaction largely proceeds by fragmentation to HCN, HNCS, and PhNCCCO (**163**).[115] The isothiazolopyrimidinethione analogs of **162** are stable under FVT conditions.

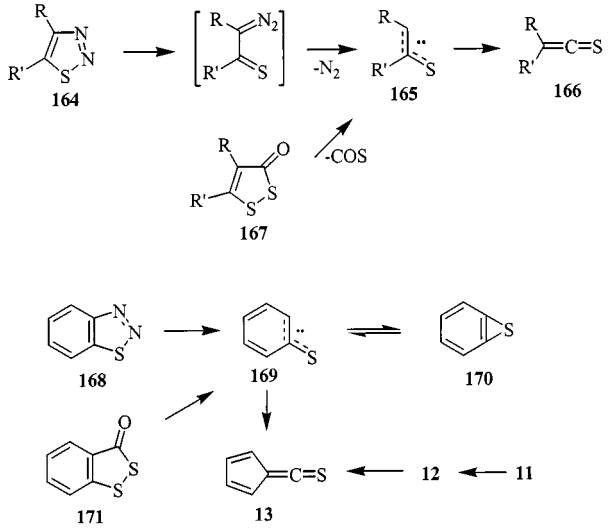
11. Thioketenes from 1,2,3-Thiadiazoles and 1,2-Dithioles

Like the pyrazoles (Section 3), 1,2,3-thiadiazoles **164** decompose, perhaps through diazothioketones, to thioacyl-



Scheme 22

carbenes or 1,3-diradicals **165**, which undergo a Wolff-type rearrangement to thioketenes **166** (Scheme 23).[116] This reaction gives very good yields of thioketenes, which are unstable compounds, prone to head-to-tail [2+2] dimerization at room temperature. The same intermediates and products are generated from 1,2-dithiol-3-ones **167**, but the yields are generally inferior.[21]

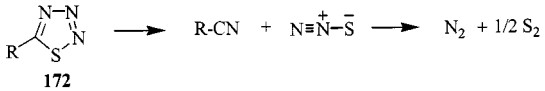


Scheme 23

Benzothiadiazole **168** generates the diradical or carbene **169**, which may exist in equilibrium with benzothiirene **170**.[117] FVT causes Wolff rearrangement to thioketene **13**.[20,21] The same thioketene is obtained by FVT of benzodithiolone **171**, or of benzothiophenedione **11**, through benzothiet-2-one (**12**) (cf. Scheme 2, Section 2).

12. Nitriles, Cyanates, and N_2S from 1,2,3,4-Thiatriazoles

Thiatriazoles **172** decompose thermally to cyanides R−CN and dinitrogen sulfide, N_2S (Scheme 24).[89] The reaction is preparatively useful for the synthesis of cyanamides, R_2N-CN, and in particular alkyl and aryl cyanates, R−O−CN. The requisite 5-alkylthiatriazoles decompose to cyanates even at room temperature in ether solution, and this is the only high-yielding and general synthesis of alkyl cyanates.[118]



Scheme 24

Conclusion

Numerous interesting compounds are obtainable by flash vacuum thermolysis, and these compounds have often not been obtained in any other way. Naturally, every method has its limitations; not everything can be synthesized by FVT. However, with the aid of careful design of starting materials, it is possible to achieve highly selective reactions, resulting in high yields of reactive molecules for deployment in further chemical reactions.

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