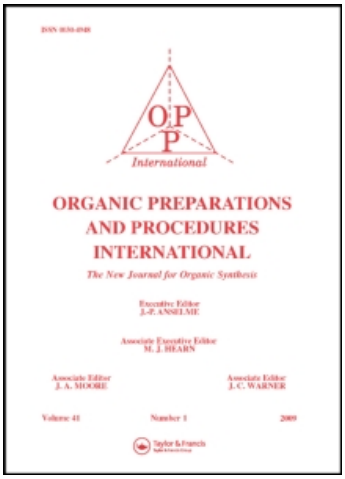

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RECENT PROGRESS IN THE PREPARATION AND SYNTHETIC USES OF THE REACTIONS OF 3*H*-PYRAZOLES. A REVIEW

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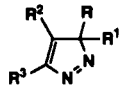
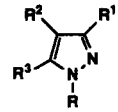
INTRODUCTION

The synthesis and reactions of 3*H*-pyrazoles (pyrazolenines) is an area of continuing interest. 3*H*-pyrazoles **1** possess a tetrahedral carbon atom in the ring and have chemical properties quite different from aromatic 1*H*-isomers **2**. An excellent and a comprehensive review has been published



1

3*H*-Pyrazoles (Pyrazolenines)



2

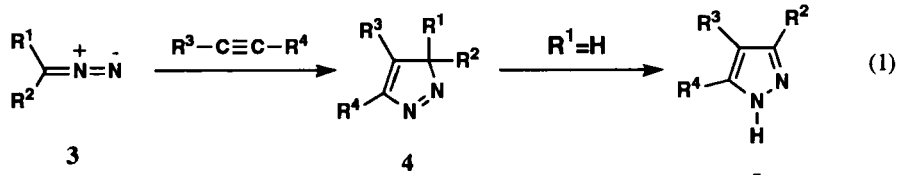
1*H*-Pyrazoles (Pyrazoles)

by Katritzky *et al.* in 1983.[1] The present survey will deal mainly with recent development of this area, including the synthesis of bicyclic 3*H*-pyrazoles, several photochemical reactions and the thermal ring opening of 3*H*-pyrazoles and also novel intermolecular rearrangements as well as well-known intramolecular [1,5]-sigmatropic rearrangements. Emphasis will be placed on the synthetic aspects of the preparation and uses of pyrazolenines.

I. SYNTHESIS OF 3*H*-PYRAZOLES

A. From Diazoalkanes and Alkynes

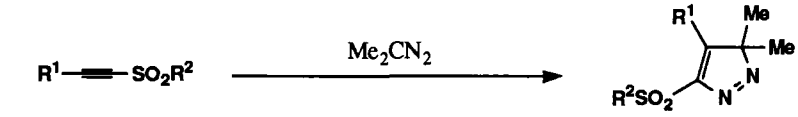
1*H*-Pyrazoles are formed when diazomethane or monosubstituted diazomethane reacts with alkynes *via* initial formation of 3*H*-pyrazoles followed by hydrogen migration to nitrogen.[2,3] When disubstituted diazomethane are employed, in general 3,3-disubstituted 3*H*-pyrazoles (pyrazolenines) can be isolated as stable adducts. The reactions of simple diazoalkanes with alkynes are HOMO (1,3-dipole)-LUMO (dipolarophile) controlled.[4] Most of 3*H*-pyrazoles have been prepared by this procedure from easily available diazoalkanes and alkynes including unreactive alkynes such as mono-[5-7] and dialkylacetylenes.[8] Attachment of both conjugating and electron-withdrawing groups on π-bond will significantly lower the energy of the LUMO and thereby accelerate reaction of dipolarophiles



3 **4** **5** (1)

with diazoalkanes. The high reactivity of dimethyl acetylenedicarboxylate (DMAD) as a dipolarophile has made it the alkyne of choice in a large number of reaction. The use of other electron-withdrawing groups such as alkoxycarbonyl,[9-26] cyano,[10,16,18,27,28] acyl,[16,18,28-30,32,33] formyl,[9,34] sulfone,[35,36] sulfoxide,[35,37] phosphinyl,[36,38,39] phenyl,[9,10,17,29,40-44] vinyl,[5,45-48] and ethynyl[49,50] has also been reported. On the other hand, 3*H*-pyrazoles may also be prepared from the reaction of an electron-rich alkyne such as ynamines, having high HOMO, with diazomethanes bearing an electron-withdrawing groups, which are controlled by LUMO (1,3-dipole)-HOMO (dipolarophile) interaction.[51-53] In general, the yields of **4** have been very high with a wide range of substituents R^1-R^4. Reactions are generally carried out at room temperature or below, and sometimes higher temperatures have been employed, but this usually results in rearrangement to the 1*H*-pyrazole.

The regioselectivity of the dipolar cycloaddition of substituted diazomethane with activated alkynes is determined both by electronic effect and by a general steric effect. In the reaction of diazoalkanes with mono or di-substituted alkynes bearing an electron-withdrawing or conjugating group such as carbonyl, phosphonyl, sulfonyl, aryl, vinyl, and ethynyl group, 5-substituted 3*H*-pyrazole **7** are favored as a result of the union of the larger diazoalkane HOMO coefficient on the carbon with that of the larger dipolarophile LUMO coefficient on the β-carbon.[4,54] Substitution of



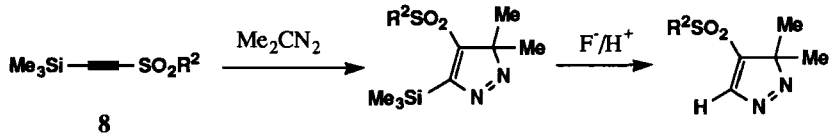
(2)

6

$R^1 = Me$ $R^2 = Ph$ $R^1 = R^2 = Me$
$R^1 = Ph$ $R^2 = Me$ $R^1 = R^2 = Ph$

7

83-96%



(3)

8

$R^2 = p\text{-}MeC_6H_4$

9

98%

10

93%

trimethylsilyl group to ethynyl sulfone or ketone causes subtle change in HOMO/LUMO coefficients or a manifestation of steric factors in cycloaddition step, resulting in the formation of a reverse orientation product **10** between ethynyl sulfone or ketone and diazoalkanes after desilylation.[55]

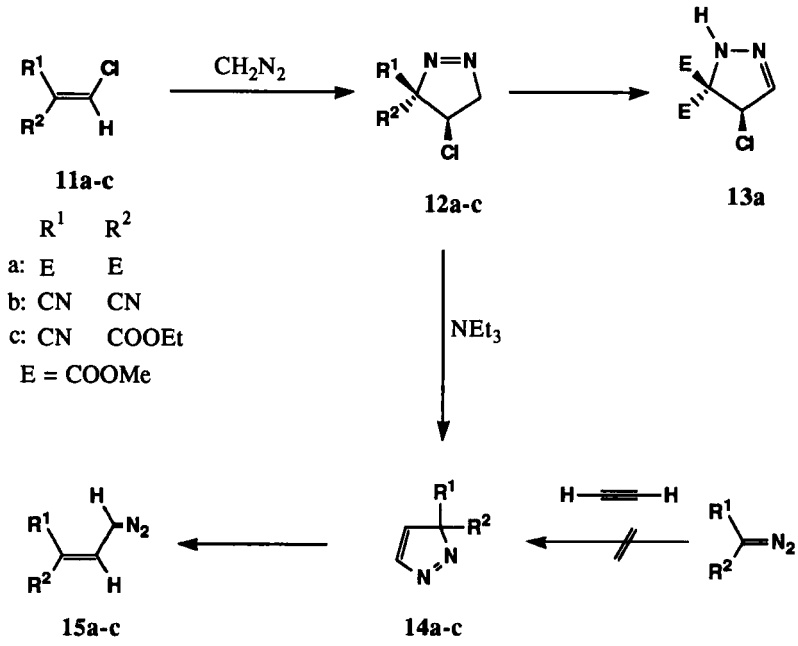
B. From Diazoalkanes and Alkenes Bearing Suitable Leaving Group

Alkenes bearing suitable leaving groups such as acyloxy,[56] amino,[57] nitro,[58] and halogen[30,31,59,96] react with disubstituted diazoalkanes to give pyrazoline with leaving groups, which can undergo elimination to give 3*H*-pyrazoles. Many examples have been described in the review.[1]

An excellent advantage of this method is useful in the system of 3*H*-pyrazole which is difficult to prepare by 1,3-dipolar cycloaddition between diazoalkanes and alkynes.

1. Pyrazolenines with Two Electron-withdrawing Groups at C-3

Reaction of 4-chloropyrazolines **12a-c**, prepared (*in situ* at -78 °C in the case of **12b,c**) from *β,β*-disubstituted vinyl chlorides **11a-c** and diazomethane, with triethylamine generated pyrazolenines

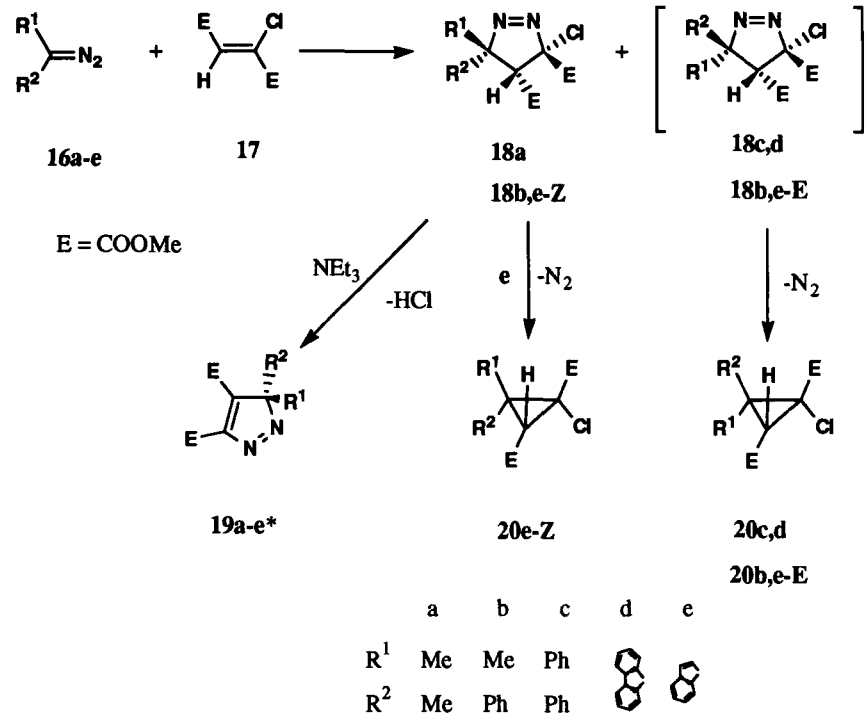


Scheme 1

14a-c bearing two electron-withdrawing groups at C-3; these cannot be prepared by 1,3-dipolar cycloaddition between diazoalkanes and alkynes. The pyrazolenine **14a** gradually underwent ring opening in competition with rearrangement of ester group, whereas, **14b,c** underwent rapid ring opening to give diazoalkenes **15b,c** in moderate yields as will be described in II-C-3.[62]

2. Use of Base as Solvent for Unstable Pyrazolines

Treatment of isolable 3-chloropyrazolines **18a** and **18b-Z**, prepared from chloroethylene derivatives **17** and disubstituted diazoalkanes **16**, with an equimolar amount of triethylamine in benzene at room temperature, pyrazolenines **19a,b** were formed in 84 and 93% yields, respectively. In the case of unstable pyrazolines **18b-E,c,d,e** which decompose to the corresponding cyclopropanes **20**, the reactions of chloroethylenes **17** with diazoalkanes were carried out in triethylamine as a solvent or in the presence of large amount of triethylamine, yielding 3*H*-pyrazoles **19**.[60,61] For example, the reaction of **16c** with **17** in the presence of an equimolar amount of triethylamine gave



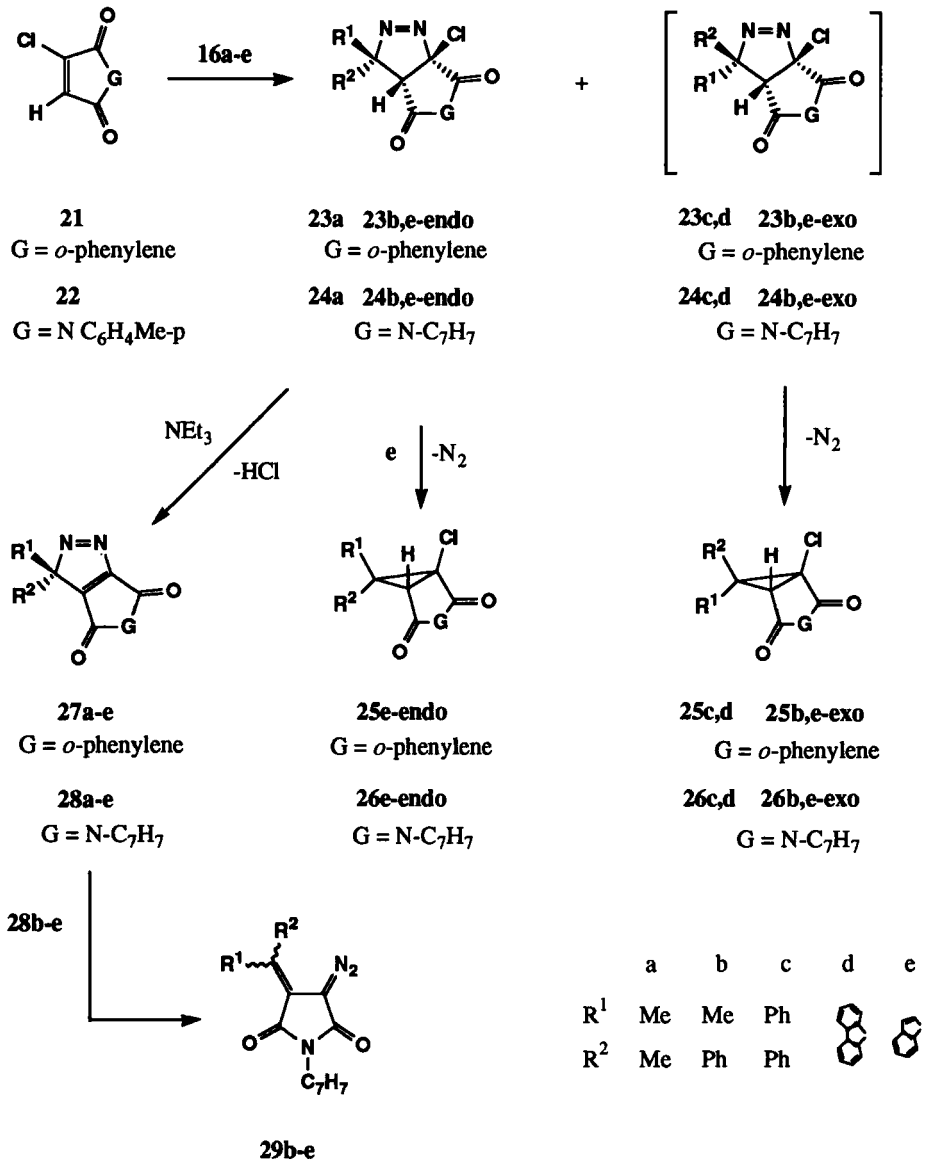
* **19e** was not isolated to undergo ring opening.

Scheme 2

19c and **20c** in 11 and 73%, respectively, while the reaction in triethylamine as a solvent afforded **19c** in 82% yield along with a trace of **20c**.

3. New Synthetic Routes to Bicyclic Pyrazolenines

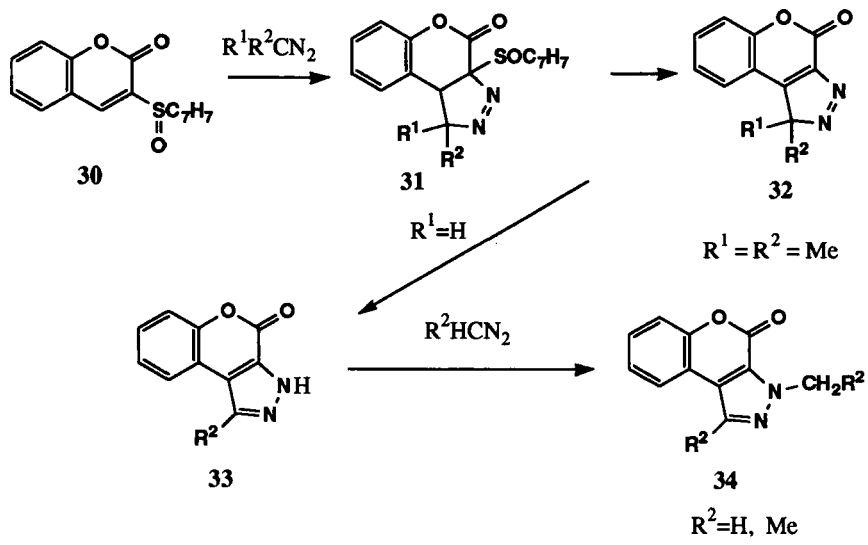
The above mentioned synthetic procedure was extended to the synthesis of bicyclic pyrazolenines which are difficult to prepare by conventional 1,3-dipolar cycloaddition between diazo compounds and alkynes because of the paucity of cycloalkynes. Bicyclic pyrazolines **23a** and **23b-endo** were treated with triethylamine at room temperature to give the corresponding 3*H*-pyrazoles **27a** and **27b** in high yield (97 and 90%) along with small amount of cyclopropanes. Since the chloropyrazolines **23c,d** obtained from chloronaphthoquinone **21** and diphenyldiazomethane or diazofluorene are too unstable to give cyclopropanes **25c,d**,[60] the reactions were carried out in the presence of large excess of triethylamine to afford the 3*H*-pyrazoles **27c** and **27d** respectively in the yields of 75 and 83%. Treatment of chloropyrazoline **24a** fused to 5-membered imide with triethylamine, gave 3*H*-pyrazole **28a** in 95% yield, whereas, 5-aryl-3-chloropyrazolines **24b-e**, prepared from aryldiazomethanes **16b-e** gave diazoalkenes **29b-e** instead of 3*H*-pyrazole.[61] The ring opening to the diazoalkenes will be described in II-C-1.



Scheme 3

4. Use of Alkenes with Sulfinyl Group

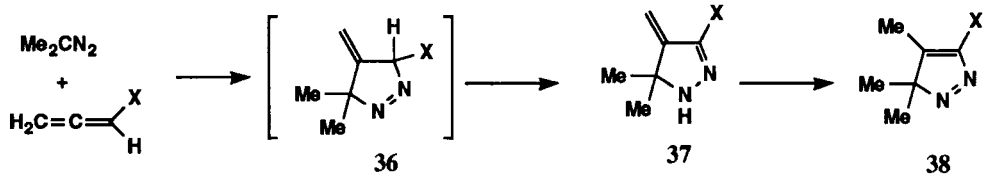
α,β-Unsaturated sulfoxides react with disubstituted diazoalkanes to give pyrazolines bearing sulfinyl group at C-3 which undergo *syn*- elimination of sulfoxide residues with the formation of 3*H*-pyrazole derivatives. Reaction of 3(4-tolylsulfinyl)coumarin (**30**) with 2-diazopropane gave 3*H*-pyrazole **32** in 91 % yield. When diazomethane or diazoethane were employed, 1*H*-pyrazoles **34** were isolated in high yields.[63]



Scheme 4

5. Use of Allenes

Methyl buta-2,3-dienoate (**35a**) reacted with 2-diazopropane in the electronically preferred sense; but in this case, the product was not the 1-pyrazoline **36a**, but the isomeric 2-pyrazoline **37a** (61% yield). Compound **37a** could be converted efficiently (85%) into the 3*H*-pyrazole **38a** by slow distillation at 0.01 mmHg.[64] The methylenepyrazoline **36b**, generated from the reaction of 2-diazopropane with phenylsulfonylallene (**35b**) gave 3*H*-pyrazole **38b** and 4-methylene-2-pyrazoline **37b** in a ratio of 4.5:1 along with bisadduct. 2-Pyrazoline **37b** underwent base-catalyzed isomerization to the major cycloadduct **38b**.[65]

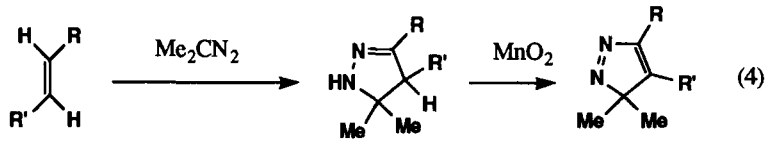


Scheme 5

C. From Oxidation of Pyrazolines

5,5-Dimethyl-Δ^2-pyrazolines (**40**) are oxidized rapidly in high yields to 3*H*-pyrazoles **41** with manganese dioxide.[66,67] This method is effective for synthesis of 5-nitro-3*H*-pyrazoles.

Generally, Δ^2-pyrazolines are prepared from diazoalkanes and alkenes, and also by the reaction of enones with hydrazine. For example, the condensation of the tertiary alcoholic enone ester **42** with hydrazine hydrate by heating in acetic acid gave the mostly pure Δ^2-pyrazoline **43** in almost

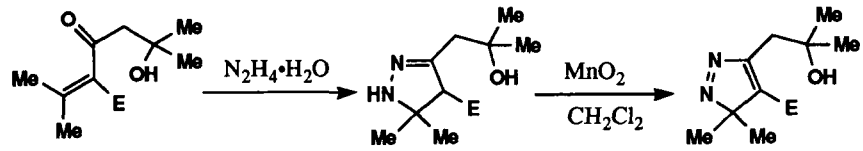


(4)

39 **40** **41**

		Yield	Yield
R = R' = CN		90	80
$R = NO_2$	R' = H	80	0
$R = NO_2$	R' = Me	50	0
$R = NO_2$	R' = Ph	88	99
$R = NO_2$	R' = CN	67	99
$R = CO_2Me$	R' = CN	46	90
R = CN	$R' = CO_2Me$	28	90
R = COMe	R' = CN	50	95
R = CN	R' = H	90	0
R = CN	R' = Me	90	0
$R = R' = CO_2Me$		95	20

quantitative yield. Oxidation with MnO_2 in methylene chloride at room temperature for 1 hr. afforded 3*H*-pyrazole **44** as the sole product.[68]



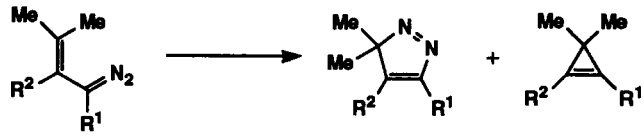
(5)

42 **43** **44**

E = CO_2Me > 95 % > 90 %

D. By Cyclization of Vinyldiazoalkanes

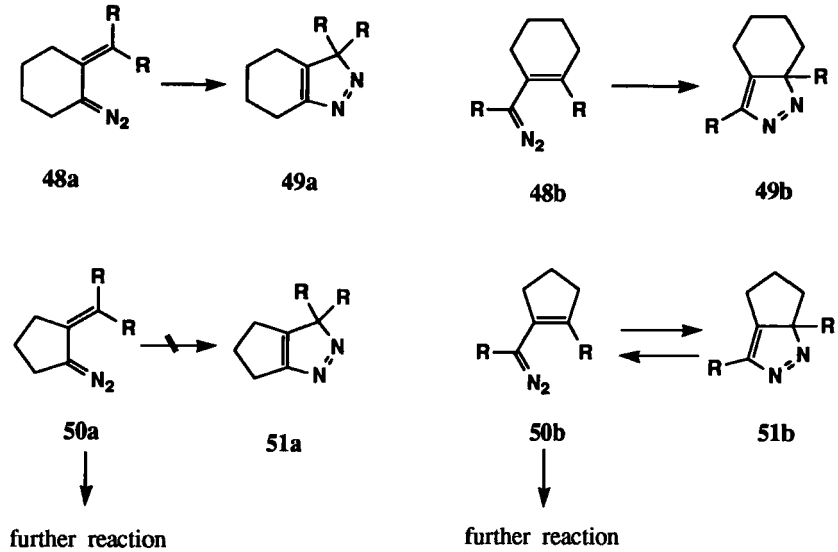
In general, vinyldiazomethanes tend to rearrange spontaneously to 3*H*-pyrazoles, although kinetic studies of this electrocyclization showed that electron-withdrawing groups especially on the α-carbon, tend to inhibit this process.[69,70,71] Cyclization of vinyldiazomethanes to 3*H*-pyrazoles is a thermally allowed process that competes with carbene formation by loss of N_2.[76] For the purpose of synthesis of 3*H*-pyrazoles, vinyldiazomethanes have been prepared by thermolysis of the alkali salts tosylhydrazones.[72-75] Vinyldiazomethanes **45** or pyrolysis of alkali salts of tosylhydrazones of α,β-unsaturated ketones gave 3*H*-pyrazoles **46** and cyclopropenes **47**.[70,72,73,77] The ratio of these two products depends on the nature of the substituents and in the case of many simple alkyl-substituted compounds, only the pyrazoles are observed.[69]



45 46 47 (6)

	Yield	Yield
$R^1 = R^2 = Ph$	70	30
$R^1 = Me$, $R^2 = Ph$	20	80
$R^1 = Ph$, $R^2 = Me$	86	14
$R^1 = R^2 = Me$	98	2

In the case of ring-fused systems, the ring size influences the course of the reaction of the diazoalkenes. For example, the systems **48a** or **48b** with six-membered ring give stable 3*H*-pyrazoles **49a** or **49b** in moderate to good yields, whereas the system with five-membered rings may give vinyldiazomethanes **50a** and further reaction products.[78]



Scheme 6

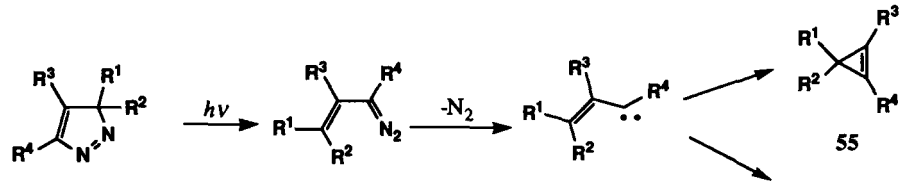
II. REACTIONS OF PYRAZOLENINES AND SYNTHETIC USES

A. Generation of Cyclopropene by Photolysis

1. Cyclopropenes

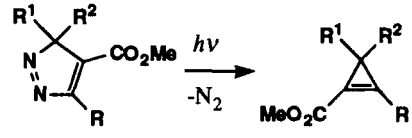
Closs *et al.* found that 3*H*-pyrazole system can serve as a convenient precursor of cyclopropenes when, irradiated with ultraviolet light.[79] In general, the photolysis of 3*H*-pyrazoles **52** is known to give diazoalkenes **53** and cyclopropenes **55** as products.[20,21,24,25,35,44,55,66,67,77,80-85] The ratio of

the two products depends on the nature of the substituents.



52 53 54 55 (7)

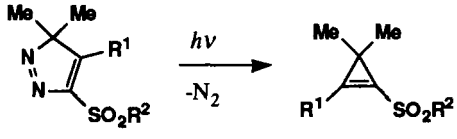
Diazoalkenes are generally isolable by irradiating 3*H*-pyrazoles with filtered light to avoid photochemical decomposition of the diazo compounds. Photolysis of 3*H*-pyrazoles in dry solvents such as benzene, ether or pentane at 320-380nm under nitrogen, using high pressure Hg lamp and filters, involving near 355nm attributed to the pyrazole ring (the N=N bond) n-π^* transition, results in isolation of the diazoalkenes (absorption 490-510nm, 2010-2090 cm^{-1}).[44,76,82] On the other hand, if the irradiation is performed with only radiation <290nm filtered out and longer wavelength radiation (>380nm) not filtered, the cyclopropenes were formed in high yields. Thus, the 3*H*-pyrazoles **56** or **58** can be photolyzed to the corresponding cyclopropenes **57** or **59**.[48,55,68,86]



56 57

		Yields
R = CO_2Me,	$R^1=R^2=Me$	70 %
	$R^1=R^2=Et$	65 %
	$R^1=Me$, $R^2=Me_2CH$	58 %
	$R^1=Me$, R^2 = cycl-Pr	60 %
R=CH_2CMe_2OH,	$R^1=R^2=Me$	95 %
R = $CH=CMe_2$,	$R^1=R^2=Me$	100 %

(8)

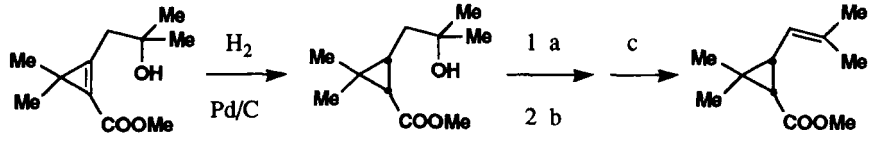


58 59

R^1=Me, R^2=Ph	97 %
R^1=Ph, R^2=Me	95 %
$R^1=R^2$=Me	94 %
$R^1=R^2$=Ph	95 %

(9)

cis-Chrysanthemate was synthesized *via* **57** (R = CH_2CMe_2OH, $R^1=R^2$ = Me) in 76% overall yield based on the corresponding 3*H*-pyrazole **56** as shown in Eq. (10).[68]



(10)

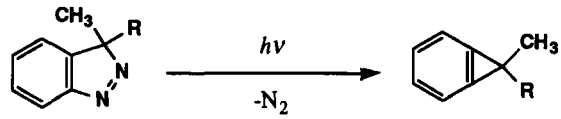
cis-chrysanthemate

a) 3.5 equiv. Et_3N ; CH_2Cl_2 b) 1.5 equiv. MsCl ; CH_2Cl_2 -5° , 20 min ; r.t., 12 hrs
c) H_2SO_4 cat. ; diox. 80° , 4 hrs

2. Benzocyclopropenes

The extension of the synthesis of cyclopropenes from 3*H*-pyrazoles to 3*H*-indazoles resulted in a convenient method for the preparation of benzocyclopropene derivatives. For example, irradiation of the 3*H*-indazoles **60** in hydrocarbon solvents at low temperatures gave the benzocyclopropenes **61** in satisfactory yields.[87]

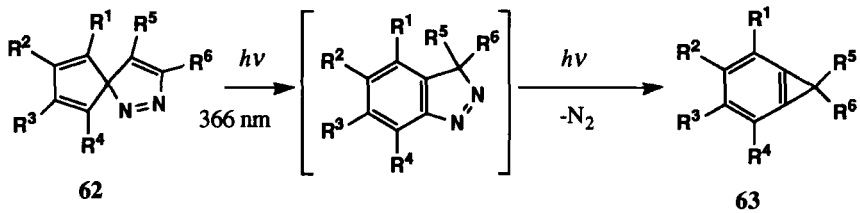
Benzocyclopropenes **63** are also obtainable by photofragmentation of diaza-(2,2)-spirenes of type **62**[88].



(11)

60 **61**

R = CN, R = $COOCH_3$, R = OCH_3



(12)

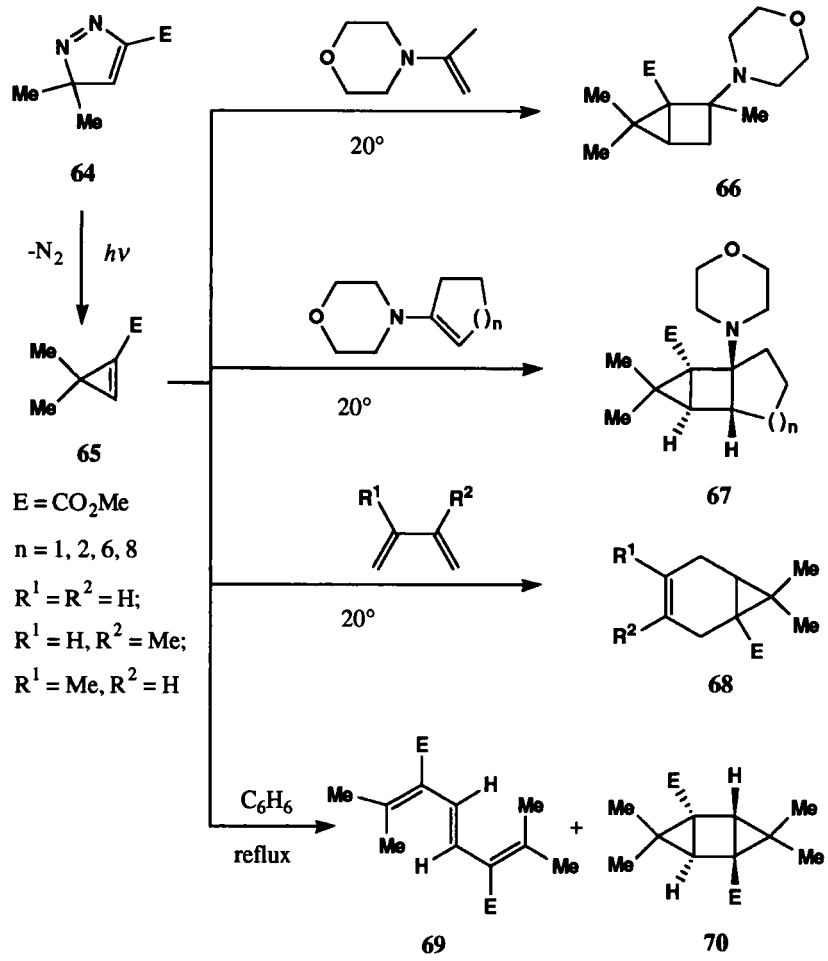
62 **63**

R^1	R^2	R^3	R^4	R^5=R^6
Ph	H	H	Ph	-$(CH_2)_6$-
Ph	H	H	Ph	-$COOCH_3$
Ph	Ph	Ph	Ph	-$COOCH_3$
Ph	Ph	Benzo		-$COOCH_3$

3. Bicyclic System *via* Cycloaddition of Cyclopropenes

Though persubstituted or 1,3,3-trimethylcyclopropenes can be isolated as mentioned above, *gem*-disubstituted cyclopropenes with a one electron-withdrawing substituent on the double bond are difficult to isolate. For example, photolysis of 3*H*-pyrazole **64** gives methyl 3,3-dimethylcyclopropene-1-carboxylate **65**, which undergoes [2+2] cycloaddition with enamines to give 2-aminobicyclo[2.1.0]pentane derivatives **66** and **67** in moderate to good yields.[89]

Cyclopropene **65** also undergoes [2+4] cycloaddition with diene to give bicycloheptenes **68** in the yields of 75-90%.[90a] On the other hand, refluxing cyclopropene **65** in benzene gave triene **69** and tricycle **70**.[90b]



Scheme 7

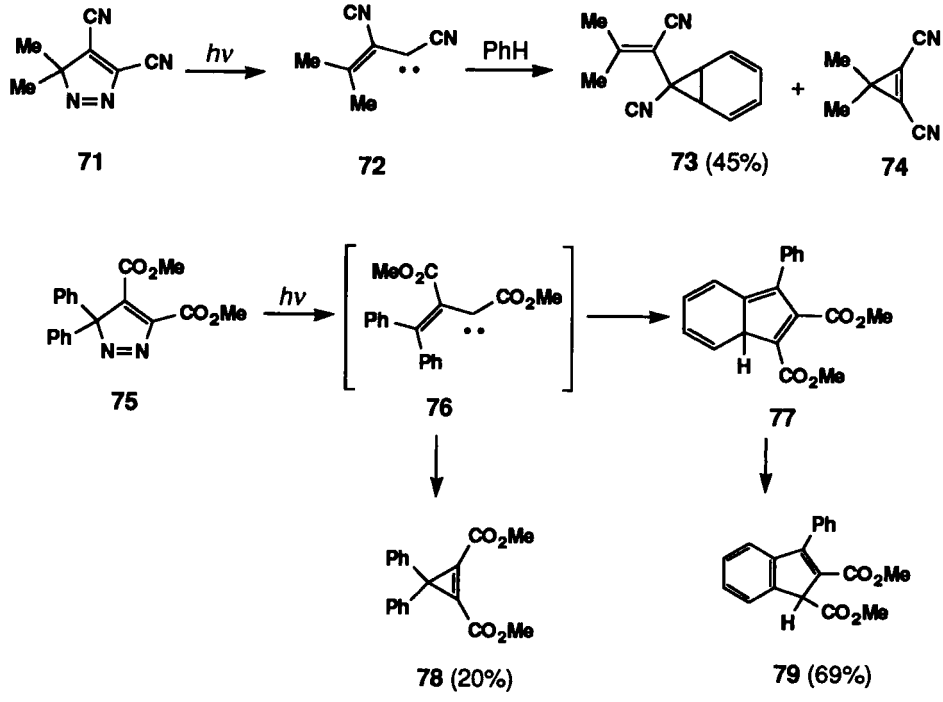
B. Generation of Vinylcarbene by Photolysis

1. Reactions Other than Formation of Cyclopropenes

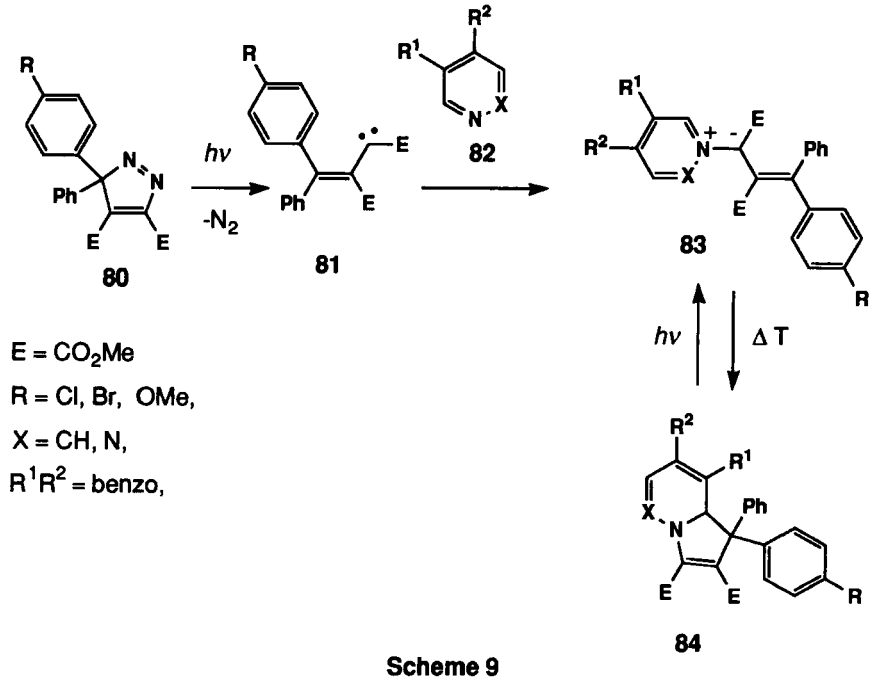
The cyclopropenes form by cyclization of the vinyl carbenes derived from the diazoalkenes accompanied with loss of N_2. The existence of the carbene intermediate has been demonstrated by trapping with reactive alkenes[35,37,91] and by intermolecular[27,91,92] or intramolecular[84,93] reaction with benzene ring as shown in Scheme 8.

The vinylcarbenes **81** derived from photoreaction of 3*H*-pyrazoles **80** were trapped with heterocycles **82** to give betaines **83** or indolizines **84** in 8-37% yields.[94]

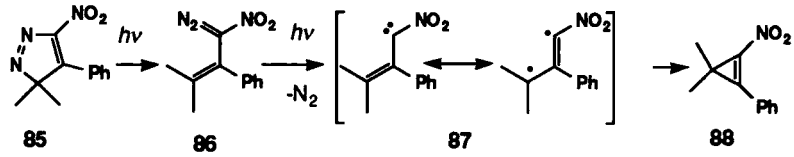
Cyclization of the vinylcarbenes to the cyclopropene ring is considered to be their most common reaction, however, this intramolecular process is not always observed and a number of competing reactions have been reported. Photolysis of nitro-3*H*-pyrazoles **85** and **92** in relatively inert

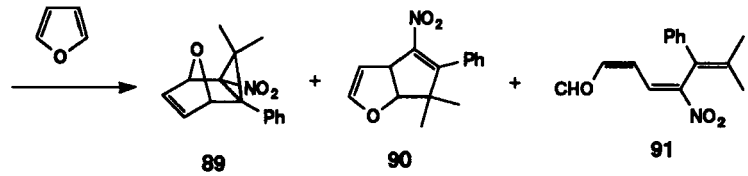


Scheme 8

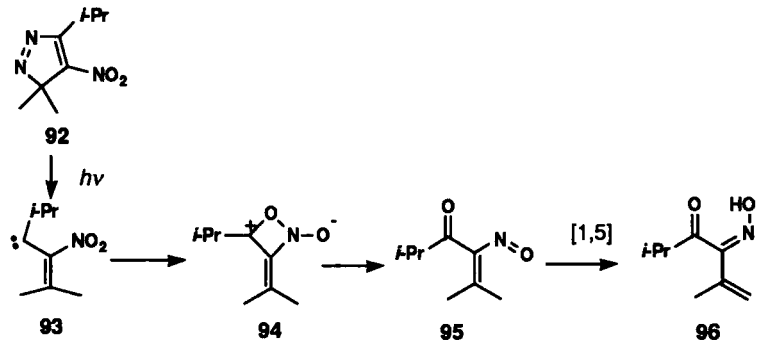


Scheme 9





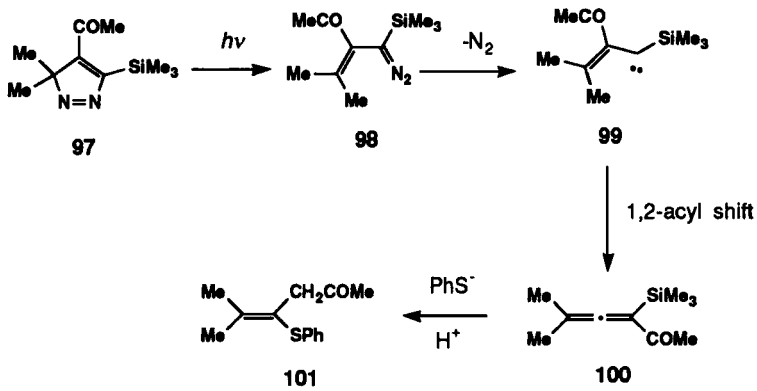
Scheme 10



Scheme 11

solvent such as methylene chloride or ether showed different behavior (Schemes 10 and 11). Intramolecular process to cyclopropene **88** is observed in the case of an α-nitrovinyl carbene **87**. In contrasts β-nitrocarbene **93** reacts with conversion of the nitro group to give α-oximinoketone **96**.[67]

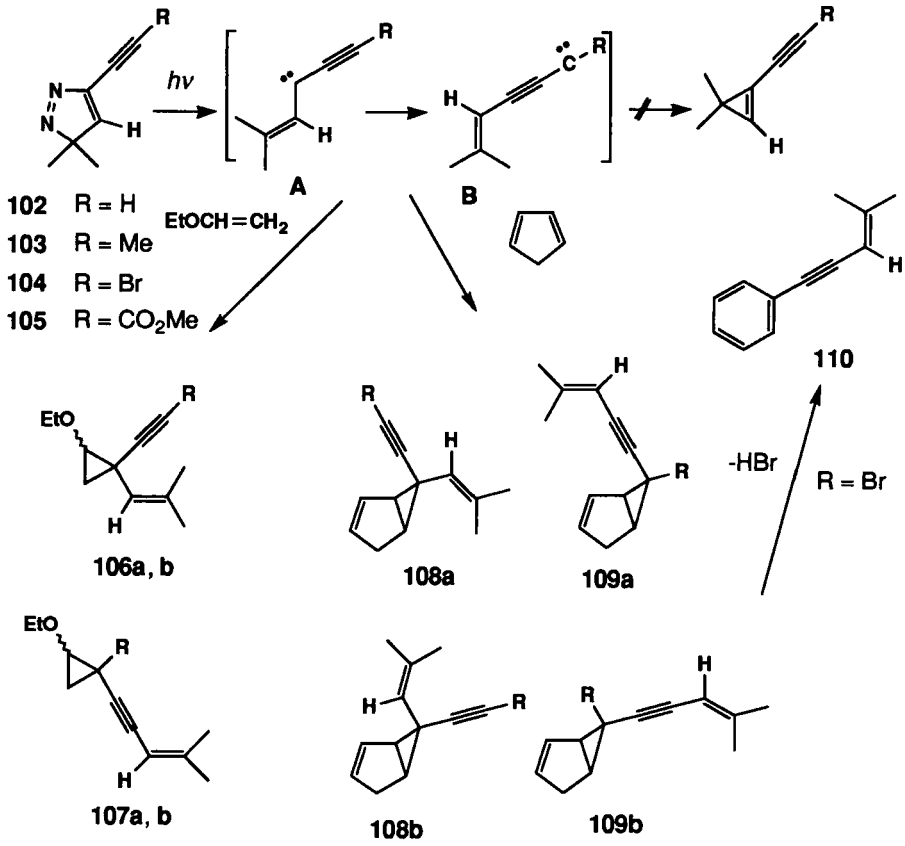
Photolysis of 3*H*-pyrazole **97** in benzene afforded allene **100** in nearly quantitative yield, by mechanism involving 1,2-acyl shift in vinyl carbene **99**.[55]



Scheme 12

2. Alkynyl Vinylcarbene (Carbene-Carbene Interconversion)

Photolysis of different 3,3-dimethyl-5-alkynyl-3*H*-pyrazoles **102-105** in vinyl ether or in the presence of cyclopentadiene gave cyclopropanic derivatives resulting from two carbenic species (**A** and **B**) whose relative reactivity depends mainly on the nature of substituent (R) of the triple bond. The results are summarized in Scheme 13 and Table 1.[49a]



Scheme 13

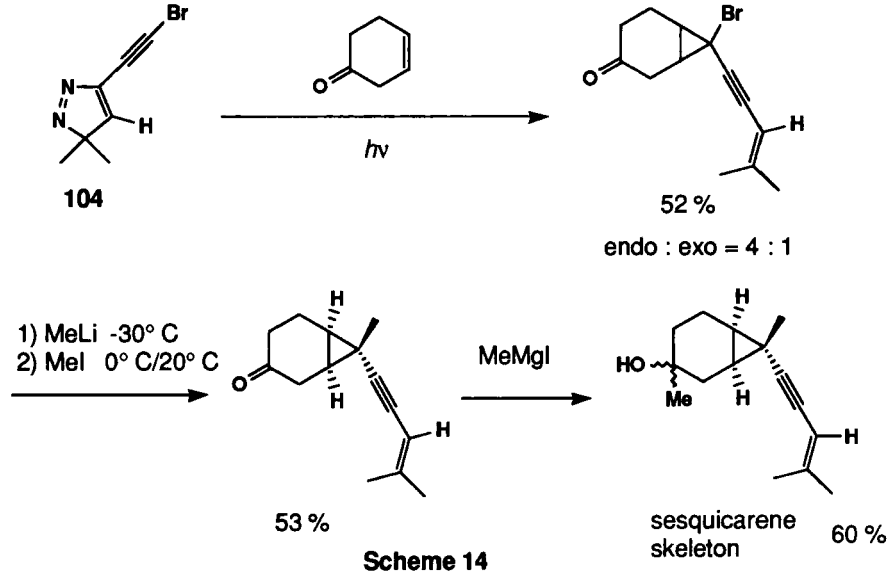
For example 3*H*-pyrazole **102** (R=H) with vinyl ether gave 65% of a 34 : 66 mixture of cyclopropanes **106** (derived from carbene **A**) and **107** (derived from carbene **B**) whereas **104** (R=Br) gave 80% **107** as sole products. Similarly, **102** with cyclopentadiene gave 80% of a 24 : 76 mixture of **108** (derived from **A**) and **109** (derived from **B**) whereas **105** (R = CO_2Me) gave 90% **109a** (derived from **B**) only. **109b** (R = Br) isomerized to give **110** accompanied with HBr elimination.

TABLE 1. Product Distribution on Photolysis of Alkynylpyrazolenines in the Presence of Vinyl Ether or Cyclopentadiene.

Pyrazolenine	R	Proportion (%) of Adducts *via* A	Proportion (%) of Adducts *via* B	Total yield(%)
102	H	34%(**106**$_a$+**106**$_b$ 1:2.2)	66%(**107**$_a$+**107**$_b$ 1:1.5)	65
103	Me	100%(**106**$_a$+**106b** 1:1.4)	—	24
104	Br	—	100%(**107**$_a$+**107**$_b$ 1:3)	80
105	CO_2Me	—	100%(>90%**107**$_a$)	90
102	H	24%(**108**$_a$+**108**$_b$ 1.3:1)	76%(**109**$_a$+**109**$_b$ 3.6:1)	80
103	Me	71%(**108**$_a$+**108**$_b$ 1.5:1)	29%(**109**$_a$+**109**$_b$ 1.4:1)	60
104	Br	—	100%(**109**$_a$+**110** 4:1)	85
105	CO_2Me	—	100%(**109**$_a$)	90

3. Use of Isobutenylalkynylcarbene to Sesquicarene Skeleton

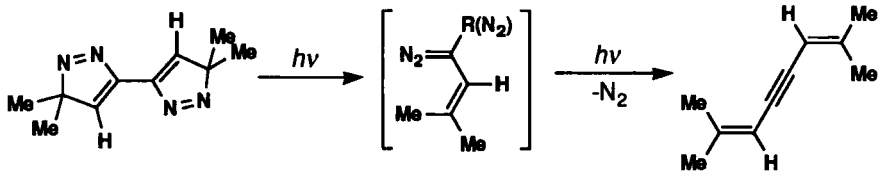
By the raction with 3-cyclohexen-1-one, the isobutenylalkynyl-carbene generated from 3*H*-pyrazole **104** can be used for convergent synthesis in the sesquicarene series as shown in Scheme 14.[49b]



Scheme 14

4. Generation of Divinylacetylenes from Bipyrazolenines

Irradiation of bipyrazolenine **111** in a variety of solvents leads to rearranged acetylenic compound **113** which on SeO_2 oxidation gave the dialdehyde in good yield (> 60%). The observed products are best explained by the intervention of unsaturated carbenes which do not cyclize into cyclopropenes.[50]

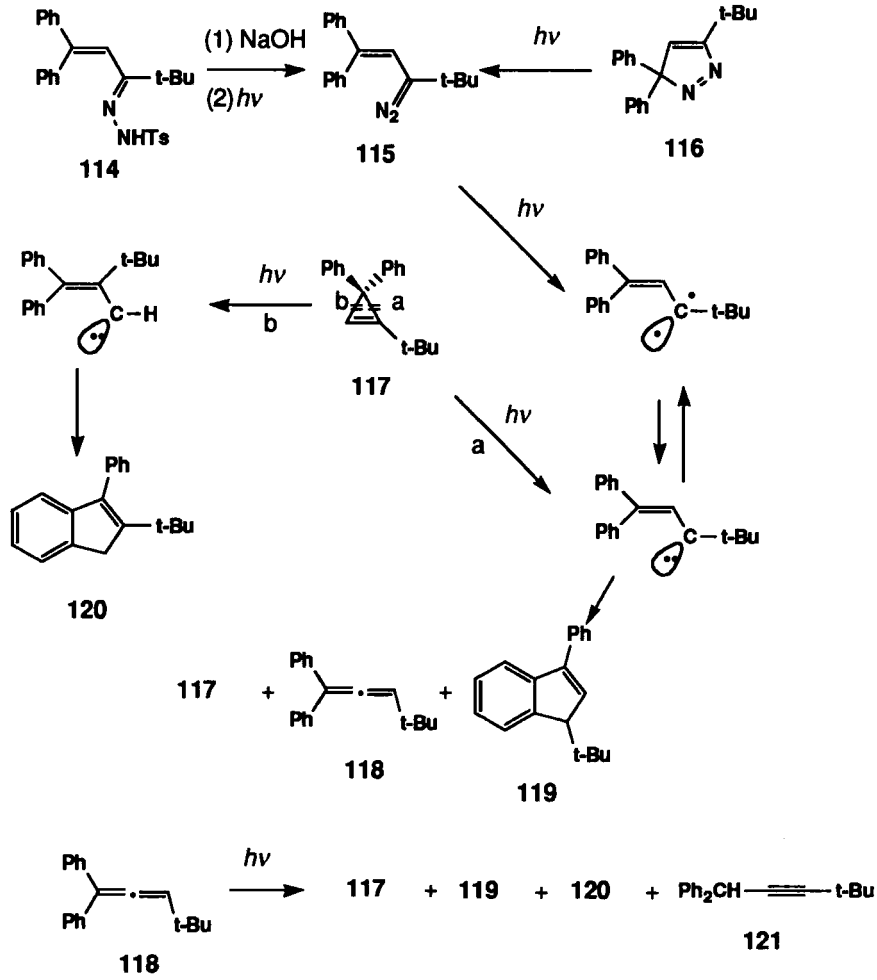


(13)

111 112 113

5. Product Distribution from Vinylcarbenes Generated from Various Sources

Some vinylcarbenes generated from 3*H*-pyrazoles have been isolated in a matrix at 5K and shown to exist as the triplet in the ground state.[25,82] The fate of vinylcarbenes generated by photolysis of tosylhydrazone **114**, 3*H*-pyrazoles **116**, cyclopropene **117**, and allene **118** is summarized in the Scheme 15 and Table 2.[75]



Scheme 15

TABLE 2. Fate of Vinylcarbene Generated from Various Sources

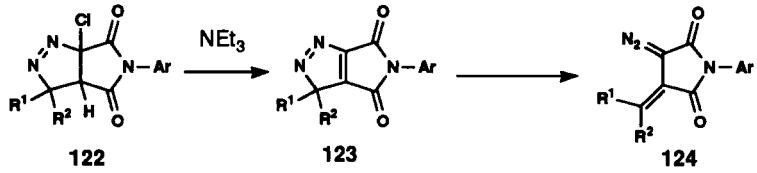
Reactant	Yield (%)					Conversion
	117	**118**	**119**	**120**	**121**	(%)
tosylhydrazone **114**	18.9	3.8	31.4	0	0	100
pyrazole **116**	29.8	4.0	43.5	0	0	100
cyclopropene **117**	45.3	4.9	19.6	3.5	0	55
allene **118**	12.9	25	21.9	2.3	13.4	75

C. Diazoalkenes by Thermal Ring Opening of Pyrazolenines

Very few 3*H*-pyrazoles were observed to undergo thermal ring-opening to diazoalkenes.[14,15,61,95] This transformation to diazoalkenes occurs only when the diazoalkenes are thermodynamically more stable than the corresponding 3*H*-pyrazoles.[62]

1. Ring Opening of Strained Pyrazolenines

3*H*-Pyrazoles **123** fused to five-membered imide ring undergo ring opening to monocyclic diazoalkenes **124**. Treatment of pyrazoline **122b-e** with triethylamine in dichloromethane at room



122 **123** **124** (14)

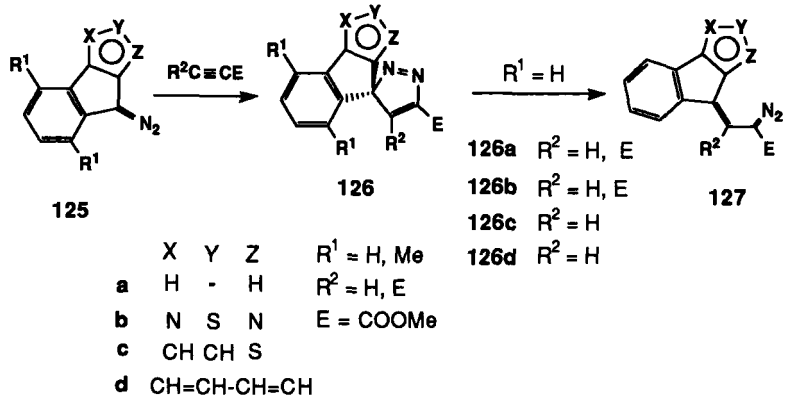
Ar = p-MeC$_6$H$_4$		**a**	**b-Z**	**b-E**	**c**	**d**	**e**
	R^1	Me	Me	Ph	Ph		
	R^2	Me	Ph	Me	Ph		
		59%	29%	44%	75%	71%	11%

temperature gave diazoimide **124b-e** instead of 3*H*-pyrazole **123b-e** in the yields as shown in Eq (14), while in the case of $R^1 = R^2$ = Me, the 3*H*-pyrazole **123a** was isolated: if could be transformed to diazoimide **124a** on heating the diluted toluene solution (1 mmol/l) in 59% yield. The ring-opening of **123** is attributed to the ring strain of the $\Delta^{1,5}$-bicyclo[3.3.0]octene system.[61]

2. Ring Opening of Pyrazolenines with Indenylidene Substituent

Mataka *et al.*[14,15] and Padwa *et al.*[95] have shown that some spiro-3*H*-pyrazoles **126** undergo ring-opening to indenylidene- or heteroaromatic fused indenylidene diazoethanes **127**. These results indicate that indenylidene groups in **127** may stabilize diazoalkenes more than 3*H*-pyrazoles. Reaction of diazoindenes **125a** and **125b** (R^1=H) with dimethyl acetylenedicarboxylate (DMAD) or methyl propiolate gave diazoalkenes **127a** (R^2 = E, 94%; R^2 = H, 38%) and **127b** (60-84%). However, when steric interaction inhibits planarity and extensive conjugation of **127**, 3*H*-pyrazole **126** is isolated. 3*H*-Pyrazole **126b** was isolated in 91% yield in the case of R^1 = Me, R^2 = E, where steric interaction

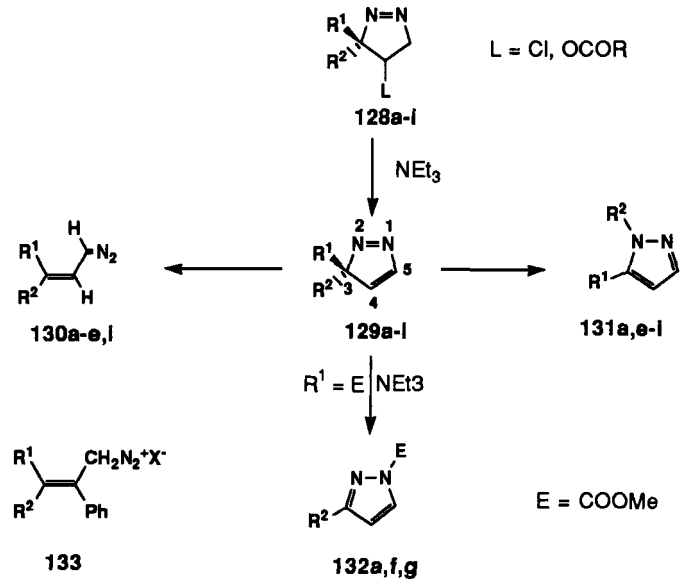
between the ester group and the methyl group of the indenothiadiazole is present. Diazo compounds **125c,d** (R^1 = H) with DMAD gave 3*H*-pyrazoles **126c,d** (32 and 100%, respectively), whereas the reaction with methyl propiolate gave diazoalkenes **127c,d** (R^2 = H) in moderate yields.



Scheme 16

3. Diazoalkenes with Electron-withdrawing Groups

The present authors[62] found that the 3*H*-pyrazoles bearing an electron-withdrawing group at C-3 underwent ring-opening to diazoalkenes in competition with sigmatropic rearrangements. Only diazoalkenes **130b-d** were obtained on treatment of pyrazolines **128b-d** with triethylamine without isolation of 3*H*-pyrazoles **129b-d**. Similar treatment of **128a** and **128e** gave 3*H*-pyrazoles **129a** and **129e** which were converted spontaneously or on heating to diazoalkenes **130a,e** with formation of 1*H*-pyrazoles as a competing reaction (Table 3).



Scheme 17

TABLE 3. Product Distribution from Pyrazolenines Bearing Electron-withdrawing Groups

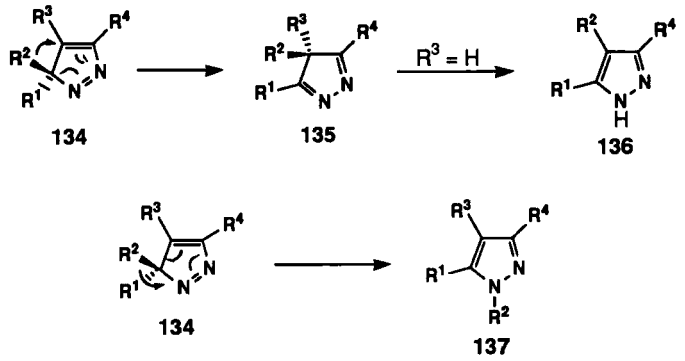
Pyrazolenine	R^1	R^2	Yield (%) 1*H*-Pyrazole	Diazoalkene
129a	COOMe	COOMe	33	24
129b	CN	CN	-	55
129c	CN	COOEt	-	40
129d	CN	p-ClC_6H_4	-	96
129e	CN	p-$ClC_6H_4CH_2$	14	73
129f	p-ClC_6H_4	COOMe	85	-
129g	p-$ClC_6H_4CH_2$	COOMe	100	-
129h	-C_6H_4-NMe-CO-(*ortho*)		76	-
129i	-C_6H_4OCO-(*ortho*)-		74	3

Carrier *et al.* obtained diazoalkene **130c** and α-phenyl derivative of **130b** and **130c** in a similar manner and explained the formation of diazoalkenes by diazonium ion intermediate **133** generated from the pyrazoline.[96,97] However, the present author's results suggest that the diazoalkenes are not formed by the diazonium ion intermediate but rather by ring opening of intermediate 3*H*-pyrazoles. These facts suggest that an electron-withdrawing group such as a cyano and methoxycarbonyl group causes thermodynamic stabilization of diazoalkenes with respect to the corresponding 3*H*-pyrazoles. This was confirmed by MNDO calculation of the heats of formation of some 3*H*-pyrazoles and their corresponding diazoalkene derivatives.[62] Thus it is reasonable to expect that as mentioned above, indenylidene groups would have a similar effect because indenylidene group has an electron-attracting property.

D. 1*H*-Pyrazoles by the van Alphen-Hüttel Rearrangement

1. Thermal [1,5]-Sigmatropic Rearrangement

As shown in Scheme 18, alkyl and aryl groups at C-3 migrate exclusively to C-4 when this atom is unsubstituted, although the benzyl group is exceptional, giving products of migration to C and N.[5,9,10,12,19,38,40,47,57b,74,98-103] In general, competitive migration occurs to C and N to give **135** and **137** for the cases where all carbon atoms are fully substituted.

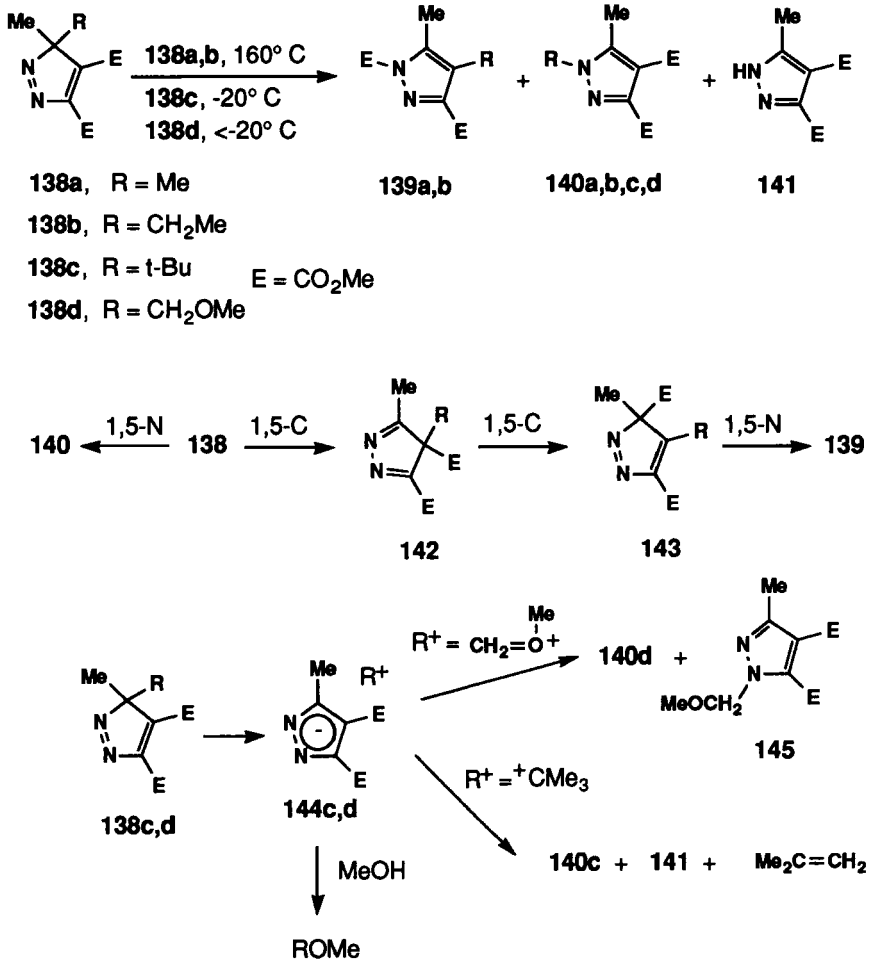


Scheme 18

When the two C-3 substituents are different, acyl group migrates more readily than alkyl,[16,104-106] benzyl[42] or aryl group.[42] This type of thermal rearrangements are commonly described as suprafacial [1,5]-sigmatropic rearrangements to denote thermally allowed concerted mechanism. These thermal rearrangements usually require high temperature in a solvent such as acetic acid, xylene or DMSO. Many examples have been described in reviews.[1]

2. Stepwise Rearrangement

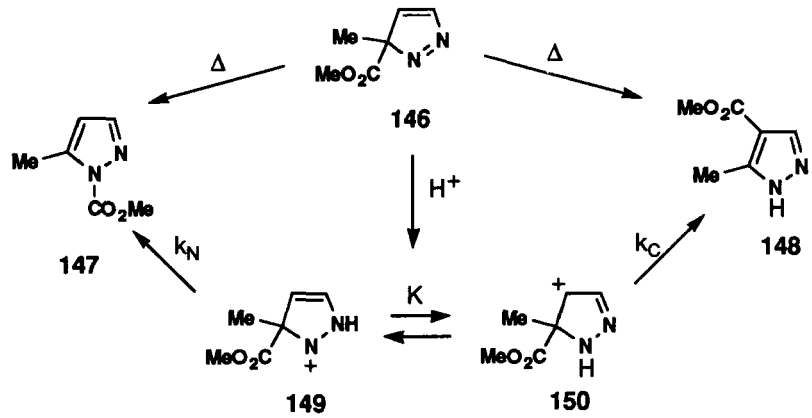
In contrast to the one step mechanism described above, there are examples of such rearrangements that require a two-step mechanism for the thermal rearrangement.[107] The evidence comes from substituent effects on rearrangement rates and from some unusual by-products. As is shown in Scheme 19, thermolysis of **138a** in benzene at 160° (sealed tube) afforded **139a** (83%), **140a** (9%)



Scheme 19

and several minor products totaling 8%. Similar normal rearrangement of **138b** occurred to afford **139b** (67%) and **140b** (33%). Those processes can be understood in terms of competitive [1,5]-sigmatropic alkyl migrations to nitrogen to form **140** and to carbon to yield an intermediate **142** which rearranges through **143** to **139** by sequential ester group migrations. In contrast to the normal behavior of **138a** and **138b**, a *tert*-Bu group in **138c** migrates much more rapidly (-20°) to give only **140c** (39%) as the product of *tert*-Bu migration, the rest going to isobutene (60%) and **141** (61%). Methoxymethyl in **138d** migrates cleanly but even more rapidly (<-20°) than *tert*-Bu. In methanol, solvent capture of *tert*-Bu to form *tert*-butyl methyl ether, competes with migration and with formation of isobutene. Similarly, methoxymethyl is diverted from clean migration by methanol solvent, which leads to formation of dimethoxymethane. These results demand a change of mechanism from the normal concerted migration to a two-step mechanism involving ion-pair formation. Presumably the stepwise rearrangement of **138** becomes important only in those cases where R^+ is a relatively stable cation and represents parts of a mechanistic continuum that runs from concerted with very little charge separation, through transition structures with considerable separation of charge, to the two-step ion-pair extreme.

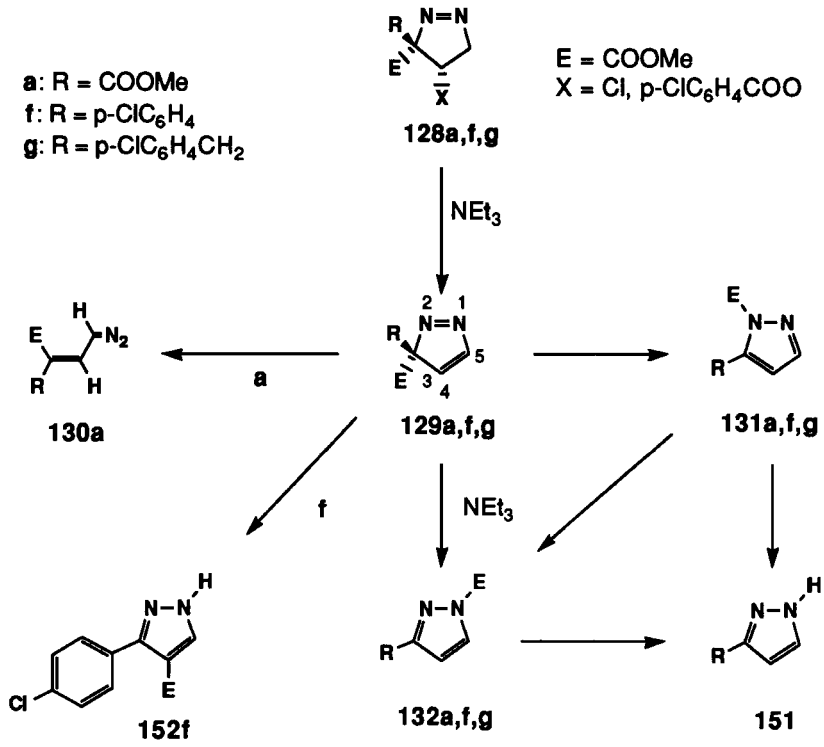
In the rearrangement of the 3*H*-pyrazole **146**, which isomerizes quantitatively to a mixture of **147** and **148** at 60°, **148** increases with increasing solvent polarity, showing that migration to carbon involved a more polar transition state. With increasing trifluoroacetic acid (TFA) concentration in dioxane as solvent, the rate of reaction increased rapidly and the isomer ratio **147**:**148** changed from 78:22 in pure dioxane to 10:90 in 5M TFA. These results were explained by assuming that the rearrangement proceed *via* **149** and **150**.[56]



Scheme 20

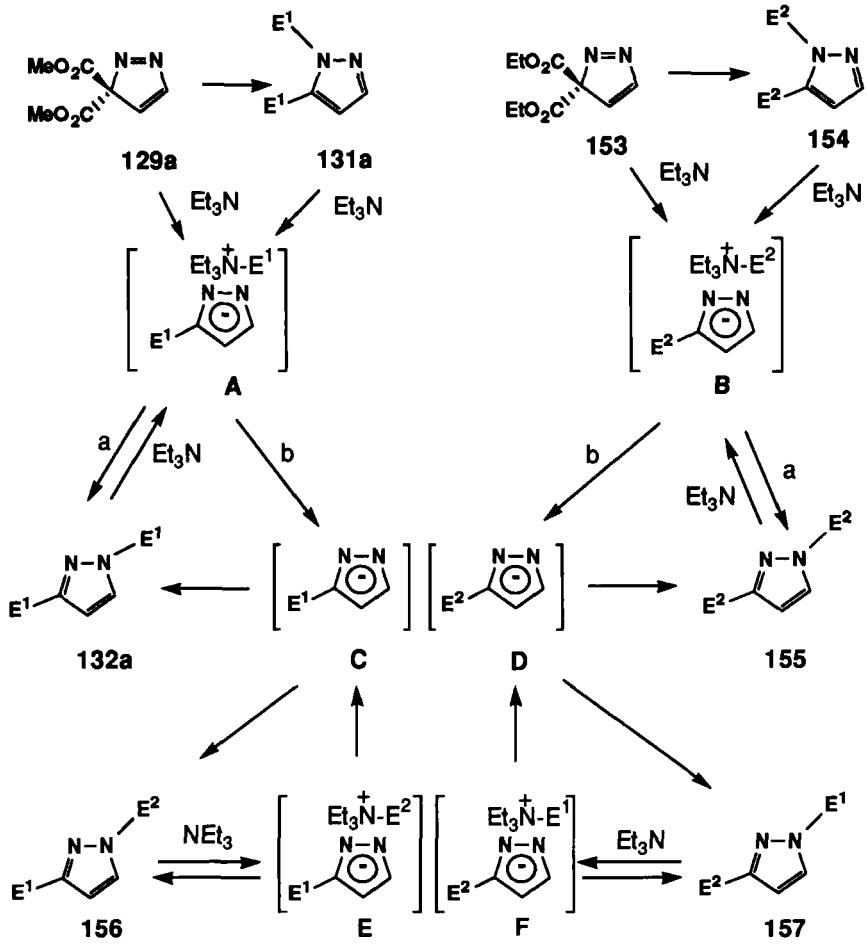
3. Base-induced Rearrangement

The van Alphen-Hüttel rearrangement has been widely recognized as a thermally allowed [1,5]-sigmatropic rearrangement. 3*H*-pyrazoles **129a,f,g** bearing a methoxycarbonyl group at C-3 underwent [1,5]-sigmatropic rearrangement to give 1*H*-pyrazoles **131a,f,g** along with **130a** and **152f**



Scheme 21

as shown in Scheme 21 (quantitatively for **131g**). However, **129a,f,g** in the presence of triethylamine underwent rearrangement to 1*H*-pyrazoles **132a,f,g**, arising from migration of the ester group to the remote nitrogen (N-1).[62] Triethylamine also catalyzed the rearrangement of 1*H*-pyrazole **131a** to **132a**, whereas transformation of **132a** to **131a** was not observed. While **131a** was stable in $CDCl_3$ at 50° for 24 hrs, in the presence of triethylamine at room temperature **131a** gave **132a** quantitatively. The rate of transformation of **129a** to **132a** is faster than that of **131a** to **132a**, which suggests that the rearrangement of **129a** to **132a** is not the result of successive [1,5]-rearrangement *via* **131a** but of a direct transformation. In the triethylamine catalyzed rearrangement of **129a** or **131a** to **132a**, it is likely that triethylamine attacks an ester group at C-3 of **129a** or at N-1 of **131a**, generating intermediate A (Scheme 22). In order to confirm whether (a) the intermediate A collapses to **132a** or (b) the pyrazole anion C diffused from the ion pair A intermolecularly attacks an ester group of **129a** or **131a** to give **132a**, crossover experiment using **129a** and 3,3-bis(ethoxycarbonyl)-3*H*-pyrazole (**153**) was carried out. It revealed initial formation of 1*H*-pyrazoles **132a** and **155** bearing equivalent ester groups, followed by formation of crossover products **156** and **157** to finally give a mixture of equal amounts of four pyrazoles **132a**, **155**, **156**, and **157**. These results mean that the formation of crossover products **156** and **157** resulted from intermolecular reaction of pyrazole anions C and D diffused from ion pair complexes A and B with **153**, **155** and **129a**, **132a**.[62]



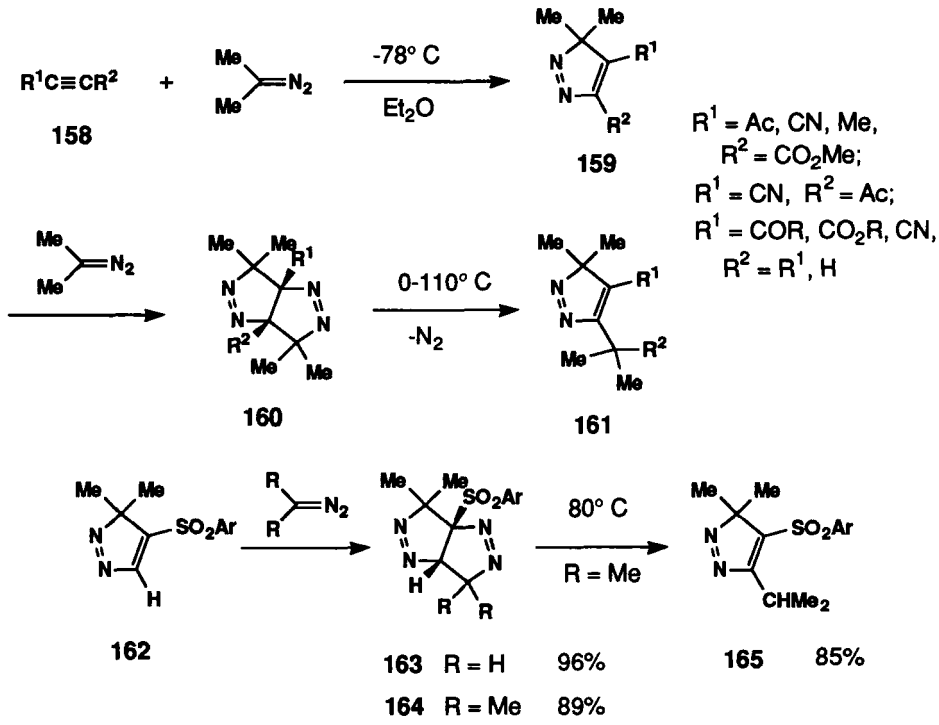
Scheme 22

E. Reactions of Ring and Substituents of Pyrazolenines

1. 1,3-Dipolar Cycloadditions

3*H*-Pyrazoles **159** having electron-withdrawing substituents (R^1 and/or R^2) act as dipolarophiles, adding a second mole of diazoalkane to result in a double 1,3-cycloaddition of diazoalkane with alkyne, giving pyrazolopyrazoles **160** in fairly good yields.[18,20,28,55,108,109]

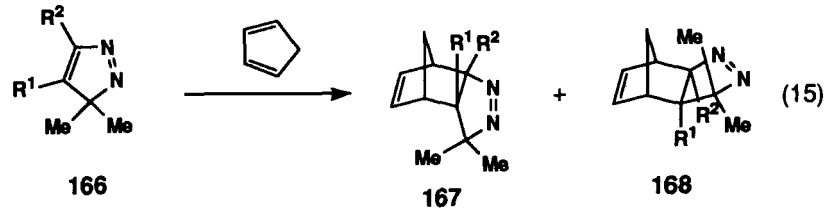
Rearrangement of **160** to the 3*H*-pyrazole **161** with loss of N_2 may also occur when $R^1 = R^2 =$ COPh at ordinary temperature (65%), but this usually requires heat.[28] The preferential loss of nitrogen from the pyrazolopyrazoles **164** with 1,2-hydrogen shift was also observed.[55]



Scheme 23

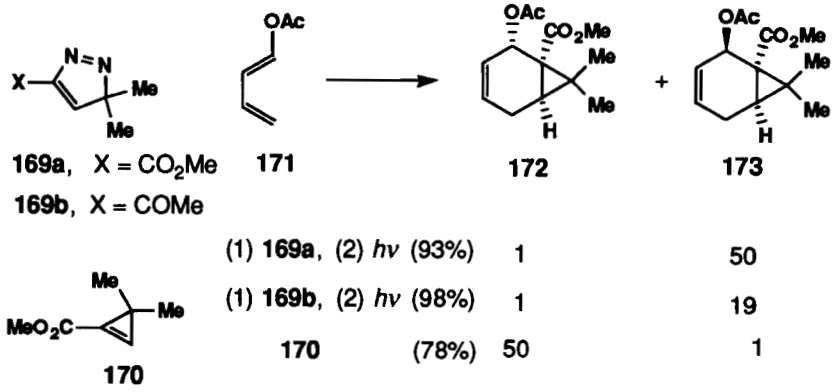
2. Diels-Alder Reactions

By analogy with the reaction mentioned above, 3*H*-pyrazoles bearing electron-withdrawing R^1 and/or R^2 act also as dienophiles at the C=C double bond. Thus **166** reacts with cyclopentadiene to give high yield of a mixture of *endo* and *exo* adducts.[110]



The 1:1 diene-cyclopropene reaction has already been discussed in II-A-3. Exposure of (*E*)-1-acetoxy-1,3-butadiene (**171**) to cyclopropene **170** (CH_2Cl_2, 10 kbar, 18 hrs) provided adducts **172** (*exo*) and **173** (*endo*) in 78% yield with an *exo*:*endo* ratio of 50:1, parallelling the established proclivity for *exo* addition exhibited by hindered cyclopropenes.

In marked contrast, 3*H*-pyrazole **169a** gave, after cycloaddition with diene **171** (CH_2Cl_2, 10 kbar, 18 hrs) and quantitative photochemical nitrogen extrusion (3500Å, 2.5 h) from the bicyclic pyrazoline intermediate, a 93% overall yield of a mixture of **172** and **173** in which the *endo* diastereomer **173** predominated in a ratio of 50:1.[111]



169a, X = CO_2Me 171 172 173

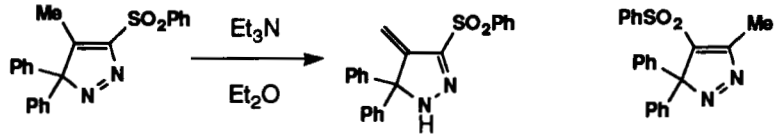
169b, X = COMe

170

Scheme 24

3. Reactions of Ring Substituents

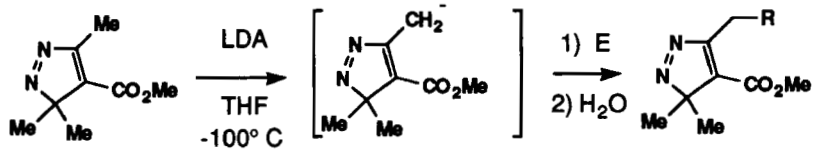
The sulfonyl 3*H*-pyrazole **174** rearranges to the methylenepyrazoline **175** in the presence of base, whereas its regioisomer **176** failed to react.[36]



174 **175** **176**

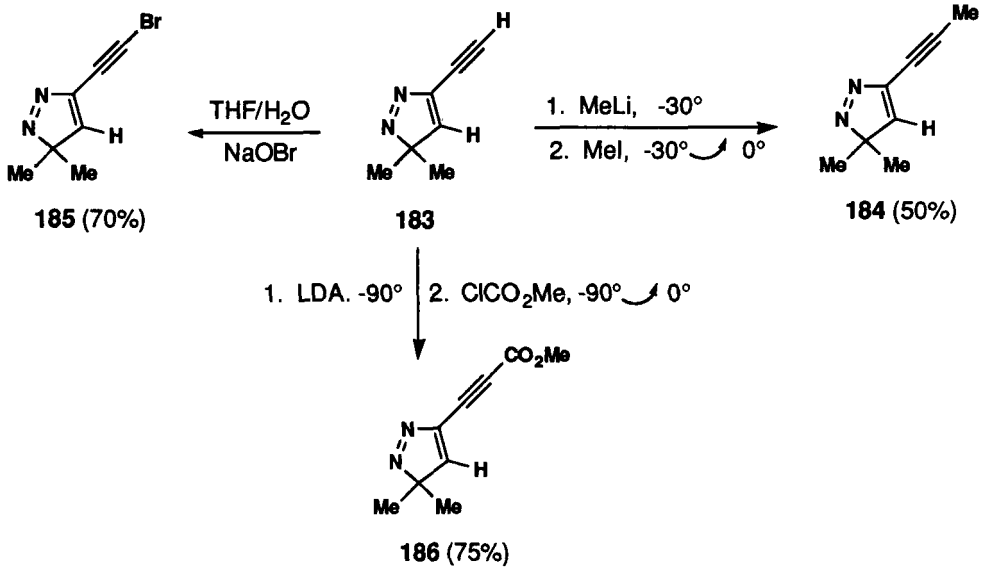
Scheme 25

4-Carbomethoxy-3*H*-pyrazoles **179-182** were prepared by deprotonation of 3,3,5-trimethyl-4-carbomethoxy-3*H*-pyrazole **177** forming an anion **178** followed by reaction with different electrophiles.[112] Similarly, different 3,3-dimethyl 5-alkynyl 3*H*-pyrazoles were synthesized from 3*H*-pyrazole **183** in moderate yields as shown in Eq. (16) and Scheme 26.[49]



177 **178** **179-182** (16)

E = Me_2CO	R = CMe_2OH	**179**	33 %
E = Ac_2O	R = COMe	**180**	43 %
E = CHO-CO_2Et	R = $CH(OH)CO_2Et$	**181**	65 %
E = $MeCOCO_2Me$	R = $C(OH)MeCO_2Me$	**182**	86 %



185 (70%) **183** **184** (50%)

186 (75%)

Scheme 26

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