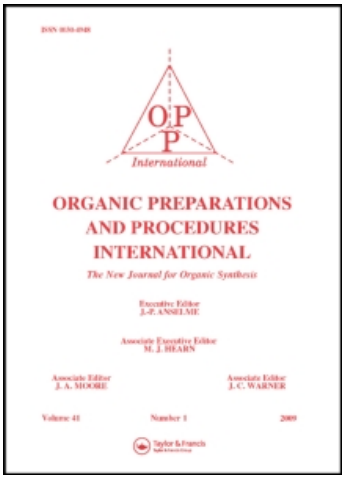

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

CONJUGATED AZOALKENES: ATTRACTIVE PRODUCTS AND VERSATILE INTERMEDIATES

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To cite this Article Attanasi, Orazio A. and Caglioti, Luciano(1986) 'CONJUGATED AZOALKENES: ATTRACTIVE PRODUCTS AND VERSATILE INTERMEDIATES', Organic Preparations and Procedures International, 18: 5, 299 — 327
To link to this Article: DOI: 10.1080/00304948609356836
URL: http://dx.doi.org/10.1080/00304948609356836

ORGANIC PREPARATIONS AND PROCEDURES INT. 18(5), 299-327 (1986)

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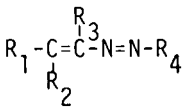
1. INTRODUCTION AND SCOPE

Compounds bearing an azo group adjacent to non-benzenoid carbon-carbon double bonds are currently called conjugated azoalkenes or azoölefins. Compounds in which the azo group is conjugated with π electrons of aromatic carbon-carbon double bonds, e.g. the arylazotropolones,[1] will be not included in the present review, even if some chemical properties of these latter compounds are related to those of conjugated azoalkenes. It is especially during the last twenty years that the chemistry of conjugated azoalkenes has been more widely investigated. In fact, with exception of a few very early papers,[2] most of these derivatives have been recently synthesized and studied. Conjugated azoalkenes deserve much more attention in view of their chemical potential. This review deals with the progress realized, during the period mentioned above, on the investigations concerning the preparation, structure, chemical and physico-chemical properties of the title compounds.

2. GENERAL CONSIDERATIONS

In every respect, conjugated azoölefins **1** (see **Scheme 1**) can be

considered part of the great family of hydrazine derivatives. Based on the type of the substituent on the azo group R_4 (see **Scheme 1**), arising from



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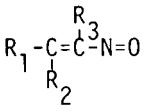


2

Scheme 1

the starting hydrazine, most of the azoalkene derivatives now synthesized can be classified and named as shown in **Table 1.**

Table 1. Classes of Conjugated Azoalkene Derivatives (**Scheme 1**).

R_4	Name
Alkyl	Alkylazoalkenes
Aryl[a]	Arylazoalkenes
SO_2Aryl[b]	Arylsulfonylazoalkenes
CO_2Alkyl	Alkoxycarbonylazoalkenes
CON<	Aminocarbonylazoalkenes
COAryl	Aroylazoalkenes
Heterocycle	Heterocyclicazoalkenes

[a] When aryl is phenyl, azoalkenes are commonly named phenylazoalkenes.

[b] When aryl is p-$CH_3C_6H_4$, azoalkenes are commonly named tosylazoalkenes.

In principle, the C=C-N=N heterodiene system of conjugated azoalkenes exhibits a reactivity analogous to that of other conjugated double bonds. The chemistry of these compounds is closely related to that of nitrosoölefins **2** (see **Scheme 1**).[3] However, the most important characteristic showed by conjugated azoölefins is ascribable to the

activating effect of the azo group on the olefinic double bond. This activating effect facilitates nucleophilic attack on the carbon atom by nucleophiles of many types, providing a variety of addition and cycloaddition reactions on the double bonds. By these reactions, various C-functionalizations and interesting heterocyclic compounds have been obtained.

3. PHYSICO-CHEMICAL PROPERTIES AND STRUCTURE

Conjugated azoalkenes are intensely colored (orange, red, amaranth or violet) products and can exist as oils, gums or crystals. Oily and gummy materials are in general less stable than those which are crystalline and tend to decompose at temperatures higher than ambient temperature and require storage in the refrigerator (-20°) in solution or as pure products under a nitrogen atmosphere shielded from light; under these conditions, no appreciable decomposition was observed for some weeks. The crystalline derivatives are usually quite stable products and can be stored for years.

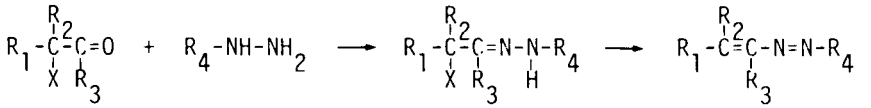
The physico-chemical and spectroscopic characteristics of conjugated azoölefins have been reported in many of the papers mentioned below, but we would like to call attention to some especially important ones here. For example, the conversion of hydrazones into related conjugated azoalkenes can be determined by IR spectroscopy. In fact, the peak in the region 3200-3400 cm^{-1} assignable to the NH group of hydrazones disappears in azoalkenes, while the band in the region 1600-1690 cm^{-1} attributable to the C=N group of hydrazones shifts to lower frequency (1520-1640 cm^{-1}), assignable to the conjugated azo-ene system of azoalkenes. In addition, a further peak at about 1450 cm^{-1} appears for azoalkene derivatives, due to the N=N group.[4] The stereochemistry of the azo-ene system has been elucidated by ^{1}H-NMR spectroscopy.[5] The pure isomers have also been separated by chromatography and/or crystallizations,[6,7] and subjected to photoisomerization.[8] In some cases, the mass spectra[9] and X-ray crystal structure[6] of conjugated azoalkenes have been discussed in detail.

4. METHODS FOR THE SYNTHESIS OF CONJUGATED AZOALKENES

The synthesis and manipulation of conjugated azoölefins sometimes present some practical difficulties, mainly because of their varying stability and reactivity. These properties usually require optimization of suitable strategies for preparation, isolation and storage (see section **3**). Conjugated azoalkenes are currently prepared from the parent hydrazone derivatives by 1,4-elimination of a good leaving group (frequently Cl^-, Br^-, RCO_2^-, Py and sometimes RSO_3^-, RSO_2^-, OH^-, F^-) on the carbon atom α-to the C=N group. This elimination has frequently been carried out by treatment of appropriate hydrazone derivatives with base. Conjugated azoalkenes have been also obtained by other reactions that in many cases are of even more specific preparative interest than those mentioned above.

a. 1,4-Elimination

Two different strategies have been demonstrated to be efficient for the successful preparation of conjugated azoalkenes. In some procedures, the leaving group (X) is attached to the carbon atom adjacent to the carbonyl group from which the parent hydrazone derivative is generated, as shown in the general **Scheme 2.**



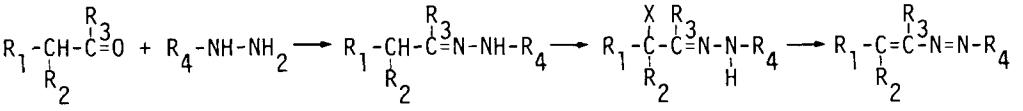
X = Cl, Br, OCOR, OSO_2R, F

Scheme 2

Thus, some of us reported the synthesis of some arylazo- and tosylazoalkenes from the respective α-bromo- and α-acetoxyhydrazone derivatives.[10-13] Subsequently, several other aryl- and arylsulfonylazoalkenes, involving various aryl- and arylsulfonylhydrazines, and different α-halo- and α-acetoxyketones or aldehydes, have been prepared by some modifications of this method.[6,7,14-24] Likewise, ß-chloro- and

ß,ß-dichloro-azoalkenes have been produced from the α,α-dichloro- and α,α,α-trichlorohydrazones, respectively.[20,25-28] ß-Fluoroazoölefins have been formed in like fashion from α,α-difluorohydrazones.[29,30] α-Chloroaldehyde and α-chloroketone methylhydrazones provided the corresponding aliphatic azoalkenes,[31-33] which have been obtained also by Zelenin et al.[34-39] Steroidal -bromophenylhydrazones afforded the related α,ß-unsaturated azosteroids.[12,40-45] The preparation of arylazoglycenosides from the corresponding α-acetate, α-benzoate and α-tosylate carbohydrate arylhydrazones has been described.[46-51] α-Chloroaminocarbonylhydrazones and α-chloroalkoxycarbonylhydrazones yielded aminocarbonylazoalkenes and alkoxycarbonylazoalkenes, respectively,[20,25,26,52-58] while α-chloroaroyl-hydrazones recently gave new aroylazoalkenes.[59]

In other procedures, the leaving group (X) is introduced on the carbon atom adjacent to the hydrazono group of the hydrazone derivative, as shown in the general **Scheme 3**.



X = Br, Py, OCOR, OSO_2R, SO_2R

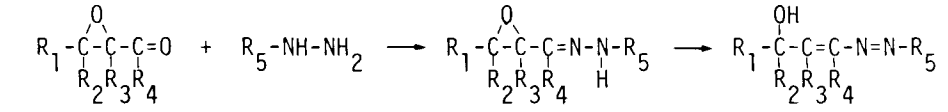
Scheme 3

Arylazoalkenes have been obtained by preliminary conversion of ketones and α-chloroketones to their α-pyridinium salts followed by alkaline treatment of the parent hydrazone derivatives.[4,32,33,60-72] The formation of phenylazoglycenosides by acylation and subsequent deacetylation of sugar phenylhydrazones have been observed.[73] Rosini et al. isolated tosylazoalkenes by reaction of tosylhydrazones with phenyltrimethylammonium tribromide followed by basic treatment in situ.[74] Some heterocyclic[75] and phosphorus azoalkenes[76] have been synthesized in analogous fashion. In a few cases tosyl or tosylate groups have been used as leaving groups in the preparation of phenylazoalkenes by the 1,4-elimination process.[9,77]

Conjugated phenylazocyclohexen-3-ones have been obtained by reaction of 1,3-dicarbonyl compounds with an excess of phenylhydrazine,[78] while 2-nitro-2-(arylazo)vinyl ethyl ethers arose by treatment of the respective arylhydrazones with triethyl orthoformate.[79] The preparation of conjugated alkyl-, aryl-, and arylsulfonylazodienes by 1,6-dehydrohalogenation of the parent α,ß-unsaturated-γ-halosteroidal hydrazones mentions merit of this route.[43,80]

b. Opening of Epoxide

The treatment of α,ß-epoxyketones with hydrazines initially produced the corresponding α,ß-epoxyhydrazones, and then α-hydroxyazoalkenes by opening of the epoxy ring, as shown in the general **Scheme 4** (see also section **5d**).[81,82] Arylazoglycenosides have been also synthesized by this method.[83]



Scheme 4

c. Other Methods

ß-Chloro- and ß,ß-dichloro-arylazoalkenes readily undergo conjugate addition-elimination reactions with amines or thiophenol in sodium hydroxide to give new azoalkenes.[20,25,27,28] Peracid oxidation of α,ß-unsaturated aliphatic azo compounds has resulted in the formation of the corresponding α,ß-unsaturated aliphatic azoxy compounds.[84] Oxidation of α,ß-unsaturated monoalkylhydrazones and bis-arylhydrazones with lead tetraacetate has been used in the generation of conjugated alkylazoalkenes and bis-arylazoalkenes, respectively.[85,86] 1-Phenylazo- and 1-phenylsulfonylazo-3-oxo-1-cyclohexenes, analogous to the compounds mentioned above,[78] have been obtained by treatment of 1,3-cyclohexanediones with the parent hydrazine derivatives.[87-89] Arylazoalkenes have been also

formed by the Wittig reaction of aldehydes with arylazomethylenetriphenylphosphoranes, generated in situ from the corresponding perchlorate salts.[90] 2,2-Diamino-1-nitro-1-arylazoölefins have been generated from the treatment of the corresponding 2,2-diamino-1-nitroölefins with aryldiazonium chloride.[91] α-Ketohydrazones repeatedly saturated with NH_3 gave 2-aminoazoalkenes, that can be reached also from reaction of enamines and phenyldiazonium chloride.[92] Conjugated azoalkenes have been frequently detected or postulated as intermediates in several reactions involving hydrazine derivatives, especially in the chemistry of osazones.[3,29,40,42-45,93-128]

5. REACTIVITY OF CONJUGATED AZOALKENES

As we will see, some studies on the chemical properties of conjugated azoalkenes are concerned with the isomeric behavior of these compounds. In other works, various chemical treatments (i.e., oxidative, thermal, solvolytic, light-induced, acidic or basic) of conjugated azoölefins have been examined in detail. However, the addition and cycloaddition of different reagents to the 1,3-double bond system of the title compounds no doubt remain the most interesting reactions of these derivatives, especially from the synthetic point of view.

a. Isomerism

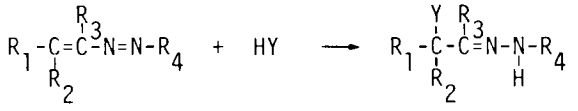
Azo-hydrazo tautomerism of conjugated azoölefins has been investigated under different conditions (see **Scheme 5**).[61,129,130,131] Similar tautomerism has been occasionally revealed for the osazone chemistry.[93,94,96,97,104,105,107,108,112,114,116] As briefly discussed in the section on physico-chemical properties and structures, the conformational isomerism of conjugated azoalkenes has been elucidated by ^{1}H-NMR spectroscopy.[5] In some cases, the pure isomers have been isolated,[6,7] subjected to photoisomerization,[8] and their crystal structures determined by means of X-ray diffraction studies.[6] Stereospecific and stereoselective behavior in the reactions of azoölefins has been frequently detected. Especially in the

1,4-conjugate additions of nucleophiles to the azo-ene system, syn and anti hydrazone derivatives have been often observed.

Scheme 5

b. Addition Reactions

As stated above, the C=C-N=N heterodiene system smoothly undergoes 1,4-conjugate addition with a wide range of nucleophiles, giving the corresponding hydrazone derivatives, as shown in the general **Scheme 6.** These 1,4-additions resulted in the functionalization of the carbon atom adjacent to the hydrazono group, and this appears to be of great interest in view of the easy regeneration of the parent carbonyl compounds from the hydrazone derivatives with one of the procedures recently reported in the literature for such purposes.[53,68-70,72,119,122,126,132,133] Thus, by combining these reactions, new and widely substituted carbonyl compounds may now become readily available.



Y = OR(Ar), SR(Ar), SO_2Ar, SeAr, NHNHAr, $CH(CO_2R)_2$, SO_3Na, $CH(CN)_2$, $CH(CN)CO_2R$, $CNHCOR(CO_2R)_2$, N_3, OCOR(Ar), NHAc, CH_2NO_2, $O(CH_2)_2OMe$, $CHAc_2$, R(Ar), H (D), NH (ND), NHR(Ar), NR_2, SAc, SCSPh, OH, CH_2SOMe_2

Scheme 6

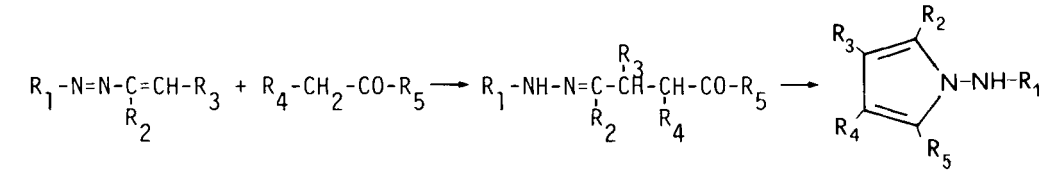
Some of us studied the spontaneous 1,4-conjugate addition of phenylhydrazine, alcohols, thiophenol and p-toluenesulfinic acid to some phenyl- and tosylazoalkenes.[10-12,129] Later, other authors reported analogous 1,4-additions in which azoalkenes were treated with alcohols,

thiophenols, benzeneselenol, and activated methylene compounds as nucleophilic agents.[60-62,72,104,123,124,126] Highly stereospecific behavior in the additions of alcohols, phenol and water to phenylazostilbene have been observed in the presence of metal ions.[134,135] Aliphatic and aromatic amines have been added to the conjugated azo-ene system of azoölefins with or without metal ions,[60,79,136,137] affording syn- and anti-hydrazone derivatives from which indole-2-carboxylic esters have been obtained, after regeneration of the parent carbonyl compounds.[53] The formation of phenylhydrazino phenylhydrazones or osazones have been also observed using phenylhydrazine or its derivatives as nucleophiles.[10,19,29,40,43,45,71, 110,118] Pyrazoles have been synthesized from conjugated fluoroazoalkenes treated with phenylhydrazine in excess, or by direct reaction of polyfluorocarbonyl compounds and phenylhydrazine in excess via intermediate fluoroazoalkenes.[29,120,121,125] The stereospecific reactions of conjugated arylazocycloalkenes with aromatic and aliphatic Grignard reagents have been extensively investigated.[66,68-70] Analogous products can be synthesized by reaction of tosylazoölefins with lithium dialkyl- or diarylcuprates.[119,122,132] Methoxide and azide ions, ammonia and amines, acetic acid, metal hydrides and deuterides, nitromethane, 2-methoxyethoxide, methylmagnesium iodide, water, sulfur nucleophiles, and the enolate derived from acetylacetone have each been shown to add to arylazoglycenosides with some differences in their relative reactivity and stereochemistry.[47-51,83] Besides the 1,4-addition, arylazoglycenosides exhibited the 1,2-addition of dimethylsulfoxonium methylide across the carbon-carbon double bond of the azoalkene, affording pyrazoline or cyclopropyl derivatives, respectively, in both cases after loss of dimethyl sulfoxide.[47,138,139] ß-Chloro- and ß,ß-dichloro-arylazoalkenes may easily undergo sequential conjugate addition-elimination reaction leading to new azoalkenes (see section **3c**) and then a further 1,4-conjugate addition to give hydrazone derivatives.[25,27,28] In the same way, ß-fluoroazoalkenes reacted in ethanol containing hydrogen chloride to yield the related 1,2-diketone

monohydrazones.[140]

The nucleophilic attack by activated methylene compounds containing adjacent ketonic carbonyl groups on the heterodiene system of the conjugated azoalkene determines the preliminary formation of the 1,4-adduct. This addition may be followed by an intramolecular condensation producing interesting heterocycles. In principle, both nitrogen atoms of the hydrazone derivative resulting from the addition mentioned above may be operative in this intramolecular condensation process, providing five-membered or six-membered heterocycles. The latter compounds, of course, are relatively unstable and suffer easy air oxidation to pyridazines. Thus, some early authors reported the synthesis of dihydropyridazines[62] that more recent investigations have demonstrated to be 1-aminopyrroles,[54,141] by means of ^{13}C-NMR[142] and X-ray diffraction study.[143,144]

Based on these findings, a synthetic strategy capable of providing a large number of 1-aminopyrrole derivatives by reaction of reactive methylene compounds (1,3-diketones, 1,3-ketoesters, 1,3-ketoamides, 1,3-ketosulfones) with various conjugated azoalkenes has been recently developed, as shown in **Scheme 7.** In a rather different way for each case,



R_1=Ar, SO_2Ar, CO_2R, $CONH_2$, CONHPh, COAr, heterocycle, $PO(OR)_2$, $P(Ph)_2$

R_2, R_3, R_5=alkyl, aryl, COOR, COOAr

R_4=COR(Ar), COOR(Ar), $CONH_2$, CONHR(Ar), $CONR_2$, SO_2R(Ar)

Scheme 7

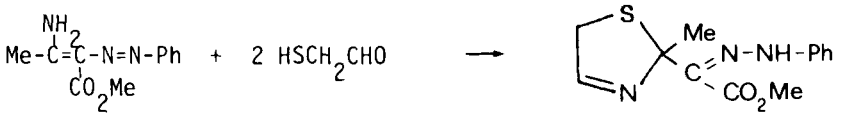
many of these reactions have frequently been observed to take place more satisfactorily under copper(II) ion catalysis. This direct preparative

procedure of 1-aminopyrrole derivatives, bearing various functional groups both at the carbon atoms of the pyrrole ring and, especially, on the amino group linked to the nitrogen heteroatom, once again demonstrated conjugated azoölefins to be powerful intermediates in organic synthesis. In fact, the aforementioned pyrroles appear not to be smoothly synthesized by any other methods.[23-25,28,54,56-58,76,141,143,145-151] Other pyrrole derivatives have been produced by (3+2) cycloaddition reactions of olefins to the 1,3-heterodiene system of conjugated azoalkenes (see section **5c**).

The 1,4-additions to give compounds with hydroxy and methyl groups on the carbon and nitrogen atoms, respectively, have been performed by treating special arylazoindolines in water and dimethyl sulfate with sodium hydroxide (see **Scheme 8**).[152]

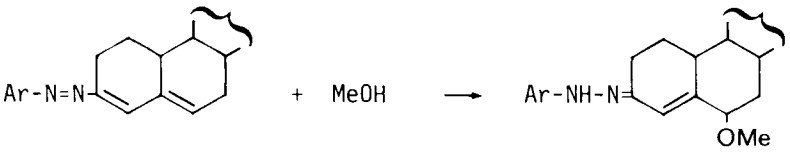
Scheme 8

Thiazolines have been manufactured from the reaction of some ß-aminoazoölefins with α-mercaptoaldehydes, likely via preliminary 1,4-addition of these latter reagents to the azo-ene system, and then by internal condensation (Asinger-type), e.g. 2,5-dihydro-2-methyl-α-phenylhydrazono-2-thiazoleacetic acid methyl ester by reaction of 3-amino-2-phenylazo-2-butenoic acid methyl ester with the dimer of mercaptoacetaldehyde (1,4-dithian-2,5-diol), as reported in **Scheme 9**.[92]



Scheme 9

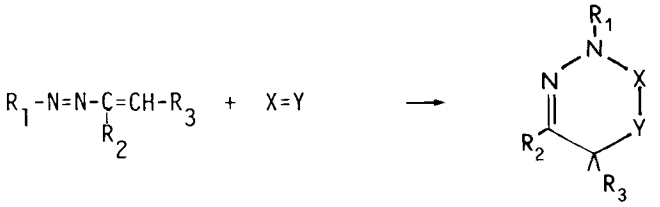
1,6-Conjugated addition of methanol to 3-arylsufonylazocholesta-3,5-dienes yielded the corresponding 6-methoxy-4-ene-3-arylsulfonylhydrazones (see **Scheme 10**).[153]



Scheme 10

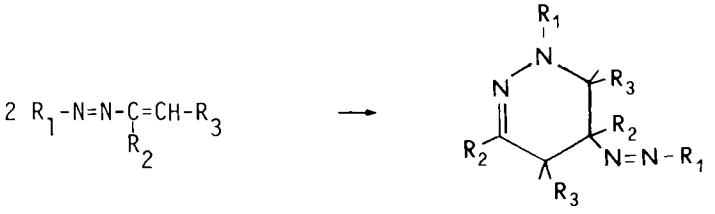
c. Cycloadditions

The 1,3-heterodiene system of the title compounds reacts readily with dienophiles and heterodienophiles of many types. With some exceptions, in the vast majority of the cases these reactions occurred in Diels-Alder fashion, producing tetrahydropyridazine derivatives (see the general **Scheme 11**).



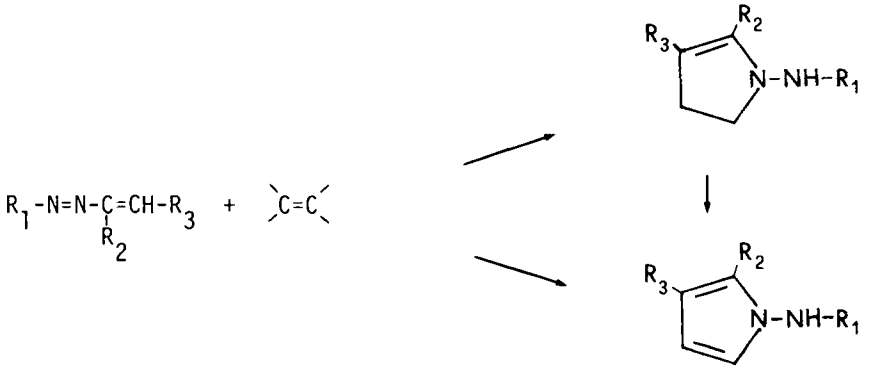
Scheme 11

In the absence of dienophiles, some conjugated azoalkenes are able to participate in (4+2) cycloadditions in both heterodiene and dienophile roles, providing tetrahydropyridazine derivatives different from those mentioned above (see the general **Scheme 12**).



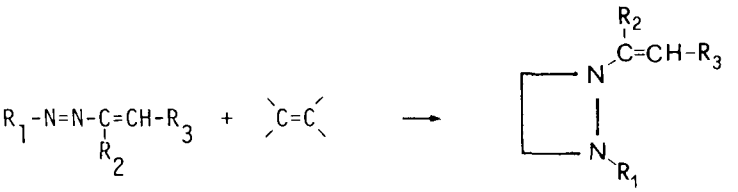
Scheme 12

In some cases, (3+2) cycloadditions between the C=C-N system of conjugated azoölefins and C=C bonds have been shown to be accompanied by (4+2) cycloadditions, giving five-membered (pyrrole type) heterocycles (see the general **Scheme 13**; see also section **5b**). There are examples in which both (4+2) and (3+2) cycloadducts are formed and others in which one or the other type of cycloadduct is formed prevalently. In fact, these reactions appear to be near the borderline between the modalities of (4+2) and (3+2) cycloaddition. Some authors recognized two distinct classes of cycloadditions of azoölefins: the case in which electron-rich azoölefins operating as electron donors react with electron-deficient olefins operating as electron acceptors, and the case in which the donor-acceptor relationship is reversed. However, the main factor which discriminates the modalities of reaction seems to be related to the ability of the substituents on the nucleophilic olefins to depress the concerted hetero-(4+2) cycloadditions in Diels-Alder fashion and encourage stepwise (3+2) cycloadditions through highly unsymmetrical transition states.



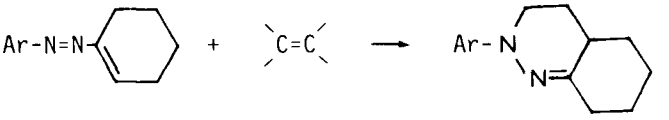
Scheme 13

Less often, (2+2) cycloadditions between the N=N bond of the conjugated azo-ene system and C=C bond have been detected concomitant with (4+2) cycloadditions, affording four-membered heterocycles (see the general **Scheme 14**).



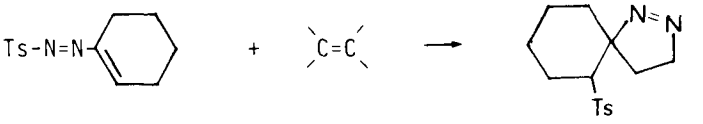
Scheme 14

Thus, some of us found that the reaction of certain conjugated arylazocyclohexenes with tetracyanoethylene and N-phenylmaleimide gave the corresponding tetrahydropyridazine derivatives by (4+2) cycloaddition (see **Scheme 15**).[13]



Scheme 15

Consistent with these general considerations and the good ability of the tosyl unit to behave as a good leaving group, the reaction of tosylazocyclohexene with various dienophiles (maleic anhydride, N-phenylmaleimide, methacrylonitrile, methyl methacrilate, ethyl methylenemalonate, citraconic anhydride) yielded pyrazolines by (3+2) cycloaddition with migration of tosyl group and spirocyclopropanes (see **Scheme 16**).[154-157]

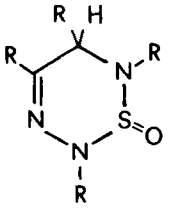


Scheme 16

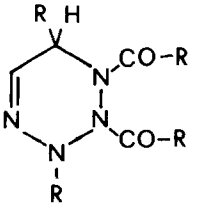
For the reasons mentioned above, conjugated azoalkenes and ß-chloroazoalkenes frequently undergo competing (4+2) and (3+2)

cycloaddition with electron-rich dienes (furan, 2,5-dimethylfuran, cyclopentadiene, 2,3-dimethylbutadiene, 6,6-dimethylfulvene, 1-methoxy-3-trimethylsilyloxy-1,3-butadiene) and olefins (cyclopentene, indene, ethyl vinyl ether, 2-methoxypropene, α-methoxystyrene, 2,3-dihydrofuran, 4,5-dihydro-2-methylfuran, 2-methyl-1-pyrrolidin-1-ylpropene, 1,3-dimethylindole, N-methyltetrahydrocarbazole), affording tetrahydropyridazines, or dihydropyrroles and pyrroles, as shown in the general **Schemes 11** and **13**, respectively.[16,20,25,26,28] Similarly, various tetrahydropyridazine derivatives have been synthesized by Diels-Alder addition of azoalkenes with a wide variety of dienophiles (acrylonitrile, methyl acrylate, methyl vinyl ketone, maleic anhydride, dimethyl fumarate, maleimide, enol ethers), as pictured in the general **Scheme 11**.[34-39,128,158,159]

Arylazoglycenosides formed tetrahydro- and dihydropyridazines by (4+2) cycloaddition of olefinic (acrylonitrile and methyl acrylate) and acetylenic (dimethylacetylene dicarboxylate) dienophiles, respectively.[138,139] Tetrahydropyridazines have been obtained in the Diels-Alder dimerization of conjugated azoalkenes, in which they behave both as heterodienes substrates and carbon-carbon dienophiles.[4,16,17,20,65,67,110,115,118,160-162] Azoalkenes reacted with dienophiles, N-sulfinyloxides and azodicarbonyl compounds by (4+2) cycloaddition to afford tetrahydropyridazines, thiatriazines (**3**) and tetrazines (**4**), respectively (see **Scheme 17**).[52,32,33]



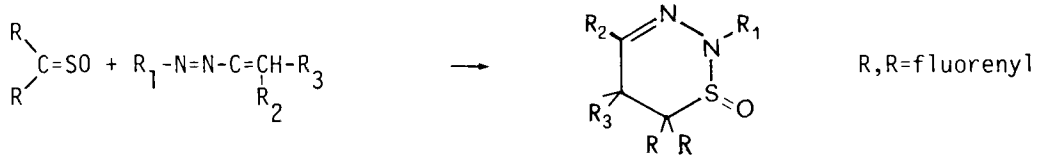
3



4

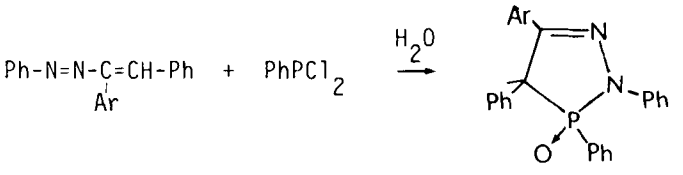
Scheme 17

Some of the structures, originally proposed for the products of the reaction of azoalkenes with enamines,[163] have since been modified and demonstrated to be pyrroles rather than pyridazines, evolving from (3+2) rather than (4+2) cycloaddition.[54,55] In addition to (4+2) cycloaddition, diphenylketenes underwent the (2+2) process, as represented in the general **Scheme 14**, providing dihydropyridazinone and diazetidinone, respectively.[18] Fluorenethione and its S-oxide underwent (4+2) cycloadditions with azoalkenes leading to the formation of thiadiazines (see **Scheme 18**).[7]



Scheme 18

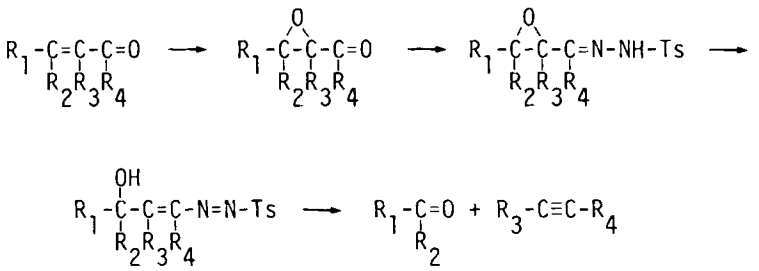
(4+2) Cycloaddition (McCormack-type) of phosphorus derivatives to the 1,3-heterodiene system of conjugated azoölefins gave new five-membered heterocycles containing the P-N-N linkage, e.g. 1,2-diaza-3,5-phospholene 3-oxide by reaction of phenylazoalkenes with phenyldichlorophosphine (see **Scheme 19**).[164-170] Diazomethane showed cycloaddition across the carbon-carbon double bond of arylazoglycenosides, producing first a dihydropyrazole ring, and then a second derivative of the same type by thermal extrusion of nitrogen followed by internal rearrangement.[139]



Scheme 19

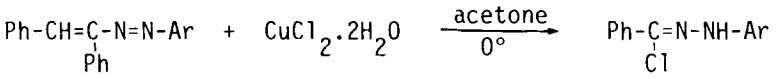
d. Other Reactions

Decomposition reactions of some tosylazoalkenes have been intensively investigated under oxidative, thermal, solvolytic, light-induced, acidic and basic conditions.[12,14,15,87,106,111,171] However, among all the reactions of this type that have been studied, the Eschenmoser fragmentation reaction presents greatest interest because of its usefulness from the preparative point of view. Generally, by this reaction it is possible to obtain both acetylene and carbonyl derivatives from α,ß-unsaturated carbonyl compounds via their related α,ß-epoxyketones. This procedure has been directly applied to the corresponding α,ß-epoxyketone tosylhydrazone derivatives. Conjugated α-hydroxytosylazoalkenes have been demonstrated to be the reaction intermediates, as pictured in the general **Scheme 20** (see also section **4b**).[98,99,101,102,109,124]



Scheme 20

Coordination complexes of transition metal ions containing as ligands conjugated azoalkenes and exhibiting coordination through a nitrogen-metal bond have also been studied.[172,173] Imidazoles and triazines have been prepared by cyclocondensation of some 2,2-diamino-1-nitro-1-arylazoethylene derivatives with homologous acyl halides.[91] Phenylazofluoroölefins have been reacted with CsF to give C- or N-alkylation, depending on the attacking substance.[30] N-(α-Chlorobenzylidene)-N'-arylhydrazines that represent very important intermediates in the chemistry of 1,3-dipolar cycloadditions have been isolated in high yields by reaction of arylazoalkenes with copper(II) chloride in acetone (see **Scheme 21**).[21,22]



Scheme 21

CONCLUSION

In this review we have attempted to bring forth the most significant progress realized in the synthesis and chemical reactions of conjugated azoalkenes within the past twenty years. Emphasis was placed on representative material published on the preparation of new azoalkene derivatives, as well as on the 1,4-additions, (3+2) and (4+2) cycloadditions of these compounds. As can be seen from the works cited, conjugated azoölefins allow various functionalizations of the carbon atom adjacent to the carbonyl moiety and are especially useful for the construction of many types of interesting five- and six-membered heterocycles, such as variously substituted pyrrole and pyridazine rings. These important synthetic objectives appear not to be readily achieved by other methods. In addition, many of the structures derived from the title compounds can profitably be used in the synthesis of natural, pharmaceutical, and phytopharmaceutical products. In our opinion, the design of new conjugated azoalkenes and the study of their reactivity seem to represent a powerful chemical thesis, well deserving more intense investigations, assuring future chemical advances.

Acknowledgments. - This work was supported by financial assistance from the Consiglio Nazionale delle Ricerche (CNR - Rome). The authors gratefully acknowledge Prof. J.-P. Anselme (University of Massachusetts at Boston) and Prof. M. J. Hearn (Wellesley College) for their helpful suggestions in this work.

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(Received March 10, 1986; in revised form May 9, 1986)