STABLE HETEROCYCLIC FIVE-MEMBERED AZOMETHINE IMINES: AZOLIUM *N*-IMIDES, TRIAZOLIDINIUM AND PYRAZOLIDINIUM YLIDES

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Abstract - This review described two types of stable heterocyclic five-membered azomethine imines. Firstly, aromatic stabilized azomethine imines (azolium *N*-imides), containing the C-N-bond in a heteroaromatic five-membered ring. Secondly, non-aromatic stabilized compounds incorporating two N-atoms of the azomethine imine moiety in a five-membered ring and an exocyclic C-atom - triazolindione azomethine imines (or triazolindione ylides), pyrazolidone azomethine imines, and their analogues. Their preparation, structures, and some reactions are considered.

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II. Synthesis and Reactions of Azolium imides (Type A)

III. Triazolidinium and Pyrazolidinium Ylides (Type B)

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I. INTRODUCTION

Azomethine imines (AMI) are 1,3-dipoles containing in the molecule =C-N-N- moiety that consists of 3-coordinated C- and N-atoms and one more N-atom which coordination number is equal to two. Although the chemistry of azomethine imines has already reviewed and main aspects of their reactivity are well represented in a few surveys,[1-8] a broad range of works published since 1983 were not incorporated neither in these reviews nor in the last issue of Houben-Weyl on this matter.[6] The primary emphasis of this paper is precisely on these publications.

Amongst the well known stabilized AMI, that could be isolated in substance of particular interest are five-membered cyclic AMI. These AMI are the most plentyful type of compounds being considered.[5] Based on exactly cyclic 5-membered AMI lightsensitive compositions were developed that exhibited photochromic

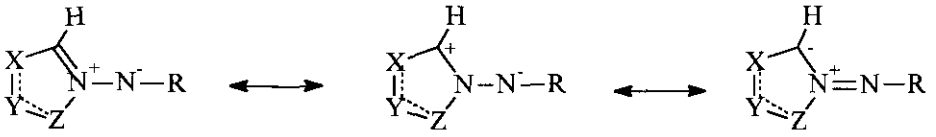
properties.[9-14] Using cycloaddition reactions of this type AMI biologically active compounds were recently synthesized.[15-18]

Whereas the chemistry of the six-membered heteroaromatic *N*-imines has been explored to a considerable extend,[1-7] there is no special review about the *N*-imines of the azoles.

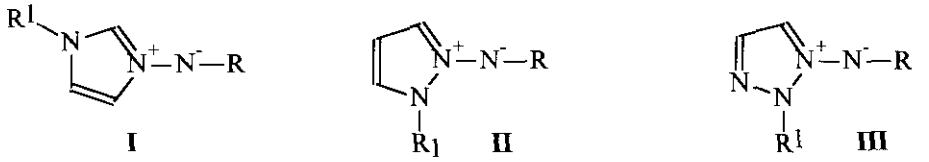
Type A: AMI which have C-N bond incorporated in heteroaromatic cyclic system. (Scheme 1)

Scheme 1

Type A



X,Y,Z: N-atoms



I **II** **III**

IV **V**

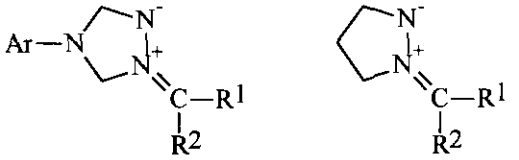
X or Z: S-atom

VI **VII**

Scheme 1 gives an overview of the main types of heteroaromatic stabilized, five-membered azomethine imines with S- and N-atoms, the so-called azolium imides.

Type B: Non aromatic 5-membered AMI. (Scheme 2)

Scheme 2

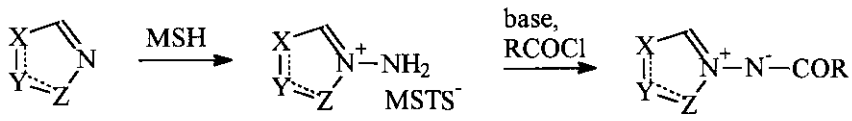


II. SYNTHESIS AND REACTIONS OF AZOLIUM IMIDES

Azolium imides exhibit high reactivity and are widely used in the synthesis of heterocyclic ring systems. The following preparative methods for the synthesis of azolium imides of the type A are described in the literature:

The most generally employed way is the *N*-amination of azoles by the use of *O*-mesitylsulfonyl-hydroxylamine (MSH) to produce *N*-aminoazolium salts, and their subsequent azolium salts using acyl chlorides or acid anhydrides in the presence of bases, for example, potassium carbonate (Scheme 3 and see II. 1., II. 2.). *N*-Arenesulfonylimides are prepared in a similar manner. Michael reagents bearing appropriate leaving groups in β-position add azolium imides with subsequent elimination of leaving group.

Scheme 3



$MSTS^-$: mesitylsulfonate

N-Aminoazolium salts may be readily altered into *N*-substituted imides by deprotonation in solution. 1,2,4-Triazolium imides are also available from 4-amino-1,2,4-triazoles by a succession of reactions; *N*-alkylation at nitrogen ring atom, acylation of exocyclic amino group and deprotonation of the 1,2,4-triazolium salt (see II. 4.).

One more synthetic approach to AMI is the direct ring closure of hydrazones by means of condensation and oxidation. By this pathway were recently also prepared heteroaromatic isothiazolium *N*-imides *via* ring closure of α,β-unsaturated hydrazones bearing β-thiocyanate group (see II. 6.). The oxidative ring closure of 1,2-dicarbonyl-bishydrazones is one more way for the synthesis of 1,2,3-triazolium-1-imides (see II. 3.). 1,3-Dicarbonyl-bisacylhydrazones give pyrazolium *N*-acylimides (see II. 2).

As one example of a ring opening - ring closure method from 1,2-dithiolium salts with substituted hydrazines is described (see Scheme 24).

Five-membered azolium imides (Scheme 1) show a variety of reactivity, depending on the nature of heteroaromatic ring and the substituents on the imino nitrogen. The most important types of the reactions are (i) reactions with electrophiles at the imino group, e.g. acylation, reaction with carbonyl compounds and in few cases following intramolecular condensation to bridgehead-nitrogen compounds, (ii) reactions

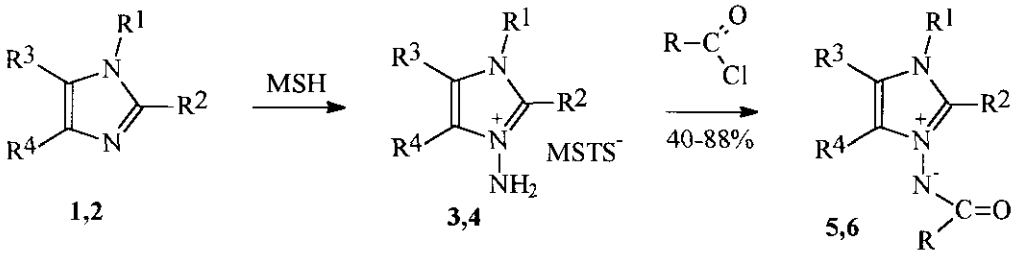
with nucleophiles on the azole ring, (iii) 1,3-dipolar cycloaddition, (iv) and N-N bond cleavage by thermolysis, photolysis and oxidation .

In the subsequent discussion on the azolium imides transformations we will consider only 1,3-dipolar cycloaddition reactions.

II.1. *1-Alkylimidazolium- and benzimidazolium-3-imides*

1-Alkylimidazoles (**1**) and benzimidazoles (**2**) were *N*-aminated with *O*-mesitylsulfonylhydroxylamine (MSH) to 3-amino-1-alkylimidazolium and benzimidazolium salts (**3,4**). Treatment of the *N*-amino compounds (**3,4**) with acylating agents like acyl chlorides, acetic anhydride, or ethyl chloroformate give stable crystalline imidazolium-3-imides (**5,6**) (Scheme 4).[19-21]

Scheme 4



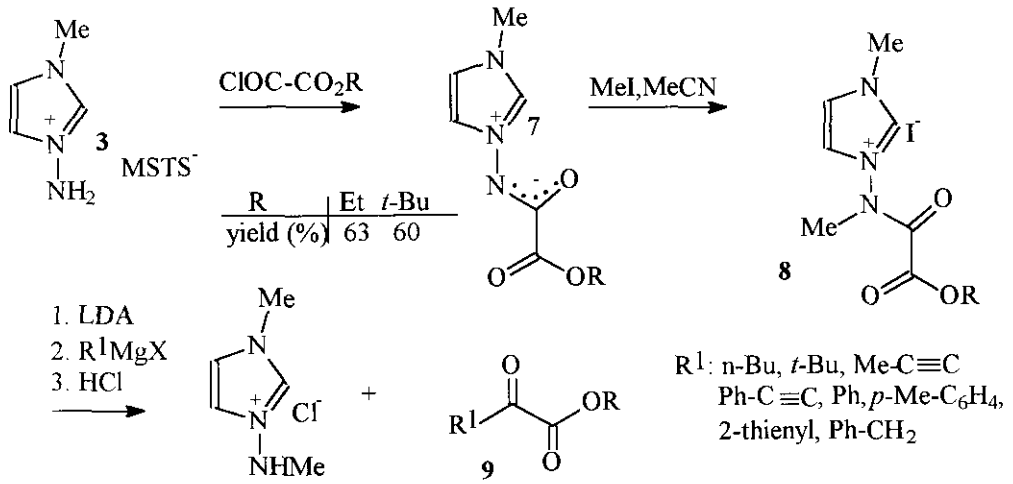
	R3	R4
1,3,5	H	H
2,4,6	(CH=CH)2	

The N-N bond cleavage to 1-alkylbenzimidazoles is the major reaction type by heating of **6** (R=Ph). Interestingly, **6** (R=Ph) gives also rearranged product to 2-acylaminobenzimidazole in addition to the N-N bond cleavage products.[19]

The use of the new oxalic ester derivatives (**8**) as selective acylating reagents done by de las Heras *et al.*[22b] provides an efficient method for the preparation of a variety of α-keto esters (**9**) *via* stable imides (**7**) (Scheme 5).

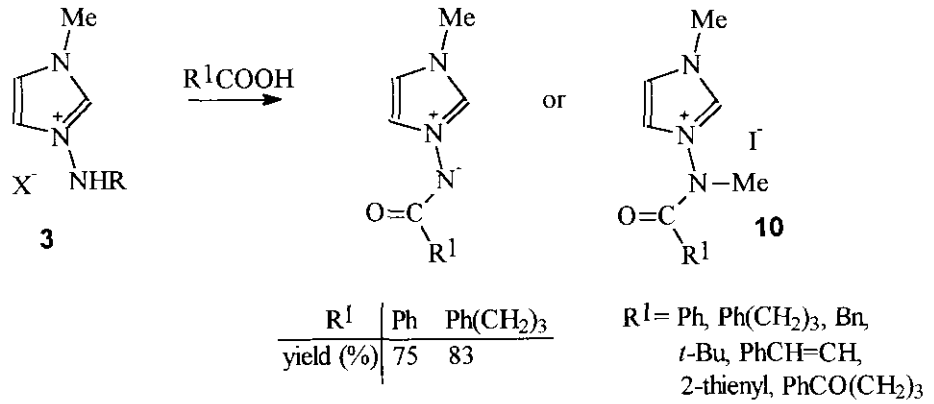
Recently, a general method was developed for the synthesis of ketones out of the salts (**3**), acyl chlorides and organolithium reagents in good yields.[21] It was also found a new synthesis of aldehydes starting with **3** by the use of diisobutylaluminum hydride (DIBALH); bis salts give dialdehydes.[22a]

Scheme 5



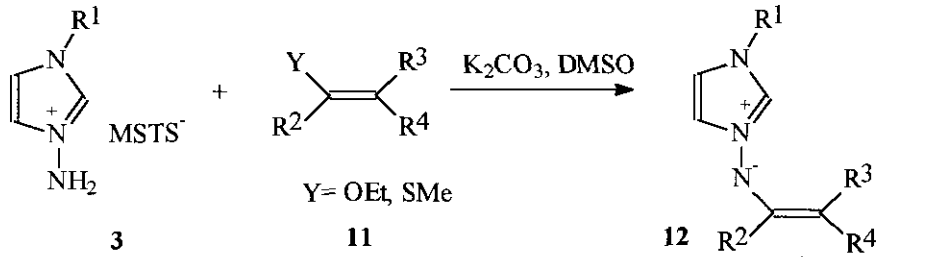
A new method for the synthesis of selective acylating agents (**10**) is described in the reaction of salt (**3**) with carboxylic acids in the presence of appropriate coupling reagents (DCC/DMAP, DEPC/NEt_3 or pyridine/oxadiazaphosphole) (Scheme 6).[23]

Scheme 6

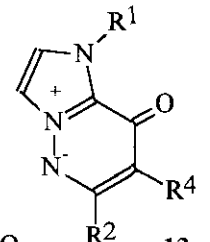


The reaction of N-aminoimidazolium salts (**3**) with polarized olefins (**11**) in the presence of potassium carbonate gave the corresponding imidazolium *N*-vinylimides (**12**). A novel 1,6-cyclisation of **12** was described to yield the betaine derivatives (**13**) (Scheme 7).[24,25] The benzimidazolium *N*-vinylimides (**4**) were investigated under a wide variety of conditions.[25] The Westphal condensation has been applied to the synthesis of quaternary aromatic nitrogen bridgehead systems by means of condensation between 2-methyl-*N*-aminoimidazolium salts (**4**) (R^2= Me), 1,2-diketones and a base.[26,27]

Scheme 7



12	R^1	R^2	R^3	R^4	yield (%)
a	Me	H	CO_2Et	CN	36
b	Me	H	CN	CN	10
c	Me	SMe	CO_2Me	CN	52
d	Bn	H	CO_2Et	CO_2Et	83
e	Bn	H	CO_2Et	NO_2	47
f	Bn	SMe	CO_2Me	CN	50

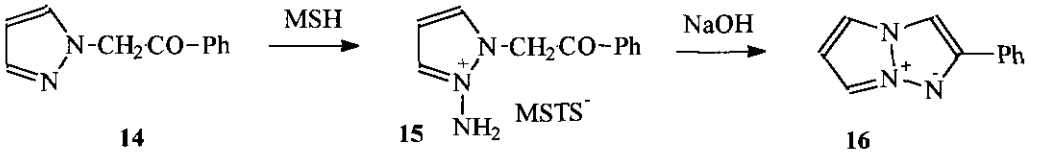


R^4= CO_2Et, NO_2 **13**

II.2. *Pyrazolium imides*

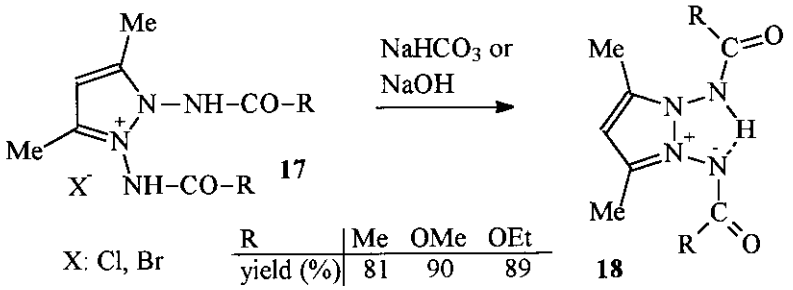
The *N*-amination reaction with MSH has been reported also for 1-phenacylpyrazole (**14**) to in situ generation of *N*-aminopyrazolium salts (**15**), the deprotonation with a base lead under cyclization to 1,3a,6a-triazapentalene (**16**) (Scheme 8).[28]

Scheme 8



Pyrazolium salts (**17**), which are easily available from 3-halogeno-2,4-dioxopentanes and substituted hydrazines in benzene at room temperature give by the reaction with sodium hydroxide or sodium bicarbonate rather stable pyrazolium *N*-acylimides (**18**) in good yields (Scheme 9).[29]

Scheme 9

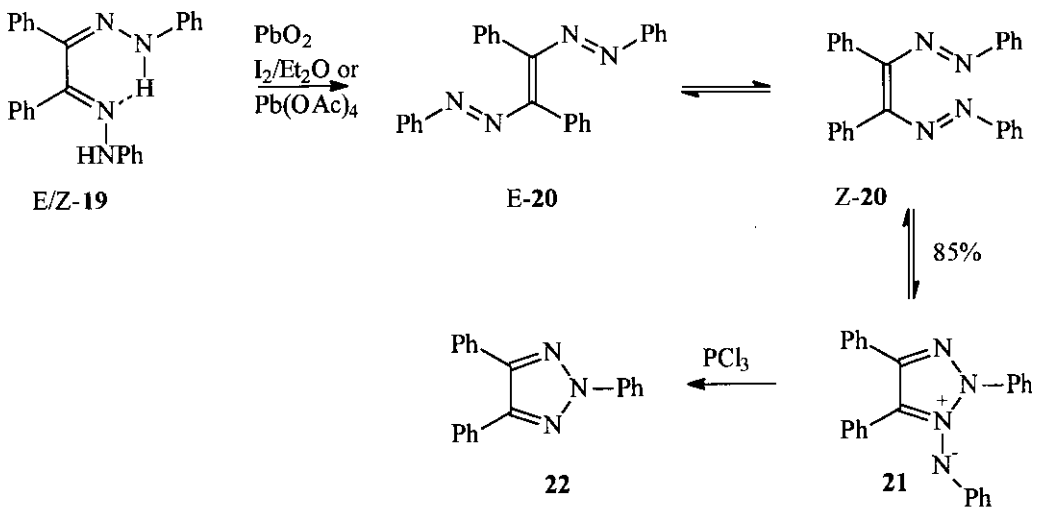


The syntheses of pyrazolobenzotriazoles under use of *N*-2-nitrophenylpyrazoles as starting compound is described by Meth-Cohn *et al.*[30]

II.3. *1,2,3-Triazolium- and 1,2,3-benztriazolium-1-imides*

The method of preparation for 1,2,3-triazolium-1-imides differ from the common methods used for other *N*-imides. A copious literature[3,8,31-46] is available about the oxidation of 1,2-bishydrazones of 1,2-dicarbonyl compounds to give stable 1,2,3-triazolium-1-imides by means of this strategy. A significant example is illustrated in Scheme 10. So the oxidation of 1,2-bisarylhydrazones ((E,Z)-**19**) leads to the formation of the corresponding 1,2-bisareneazoethylene (**20**) where the Z-form of **20** exist in dynamic equilibrium with the cyclic 1,2,3-triazolium-1-arylimide form (**21**) (Scheme 10).[8,33]

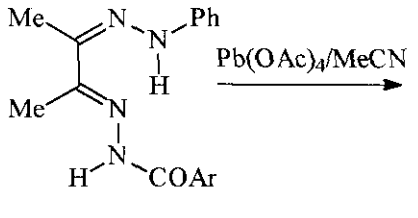
Scheme 10



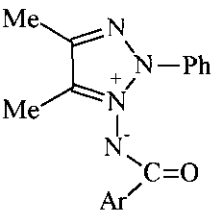
This latter form is a reactive 1,3-dipole which dominates the reactivity of these systems. The synthetic scope of **21** as a 1,3-dipole is outlined by Butler *et al.*[8] The *N*-imide (**21**) can be deaminated in quantitative yield by heating with PCl_3 to give 1,2,3-triazole such as (**22**).[8,34]

The synthesis and the oxidation with lead tetraacetate of the mixed 1,2-bishydrazones (**23**) of biacetyl result to novel stable 1,2,3-triazolium *N*-benzoylimides (**24**) (Scheme 11).[35,36]

Scheme 11



23



24

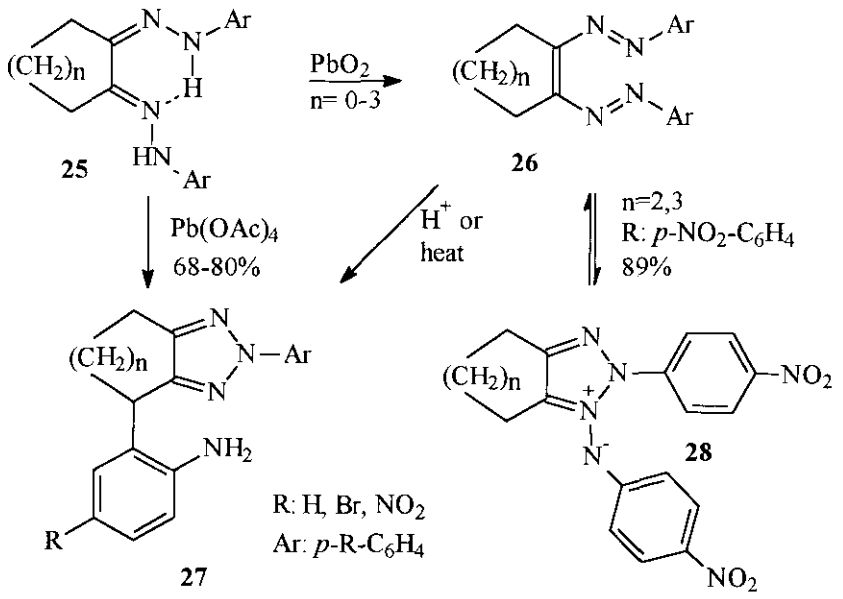
Ar	yield (%)
Ph	76
p-Me-C_6H_4	57
p-MeO-C_6H_4	32
p-Cl-C_6H_4	54
p-NO_2-C_6H_4	57

On the other hand, oxidative cyclization of 1,2-bisaroylhydrazones proceeding *via* instable 1,2,3-triazolium-1-aroylimides to 1-amino substituted 1,2,3-triazole derivatives take place.[37] Before, the structure of these products was the subject of some controversy,[3] see also.[38]

Thermolysis and photolysis of **24** in DMSO were carried out. This results suggested that benzoylnitrene was formed in the photochemical reaction. Imides could serve as non-acid aroyl nitrene precursors.[35]

Oxidation of cycloalkane-1,2-dione bishydrazones (n=2) (**25**) with non-protonic oxidizing systems such as NiO_2 in benzene or PbO_2 in CH_2Cl_2 gives **26**.

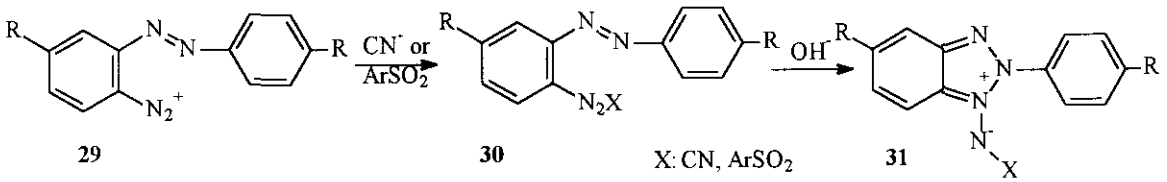
Scheme 12



If the oxidation is carried out using a protonic oxidizing system with lead tetraacetate which generated acid, the products are the rearranged compounds (**27**). This regioselective intramolecular rearrangement is a new Fischer indole-type rearrangement.[39] For 1,2-bisareneazocycloalkenes (**26**) the compounds exists perferentially in the acyclic form as indicated by their ^1H and ^{13}C NMR spectra; however, for compounds with a *p*-NO_2 substituent is present in the aryl ring, the cyclic form (**28**) becomes the dominant form (Scheme 12).[39,40]

Benzannulated stable 1,2,3-triazolium *N*-cyano- and sulfonylimides (**31**) arise from *o*-areneazodiazonium salts (**29**) and alkali cyanides or arylsulfinates, respectively (Scheme 13).[41]

Scheme 13



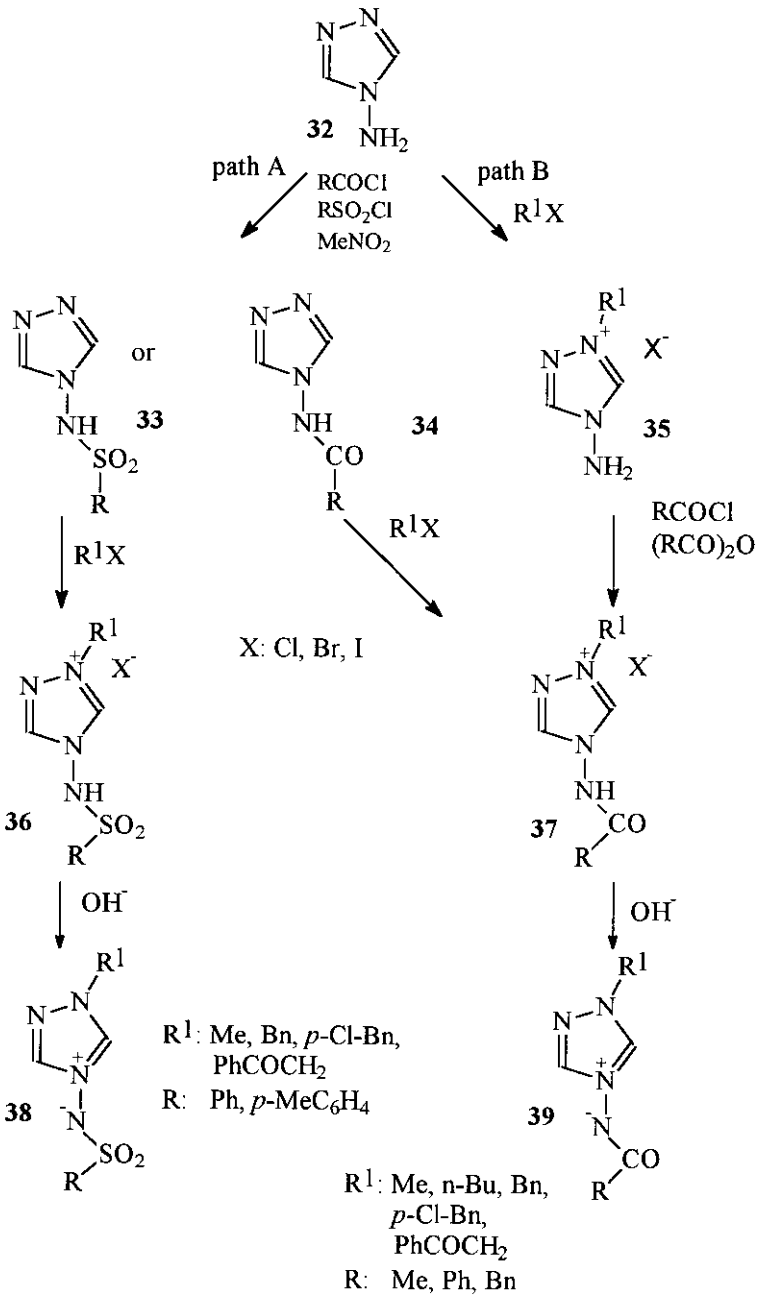
29 **30** **31**

II.4. *1,2,4-Triazolium-4-imides*

A long-known synthesis of stable 1,2,4-triazolium imides (**38,39**) is just based also on the amination of 1,2,4-triazole to **32**.[47-49] All 1,2,4-triazolium imides prepared contain the *N*-imino group in the 4-position of the triazole ring. The preparation is effected simply, and generally in good yield according to Becker's procedure,[47] by reaction of the triazolium salts (**35**) (chlorides, bromides,[47,48] tosylates[56]) with acid anhydrides or acid chlorides, then deprotonation with $NaHCO_3$ to **39** as shown in Scheme 14 (path B). 4-Amino-1,2,4-triazole (**32**) can be also acylated at the exocyclic amino group to give **34**, alkylation and deprotonation are the following steps to **39** (path A, B).[47,48]

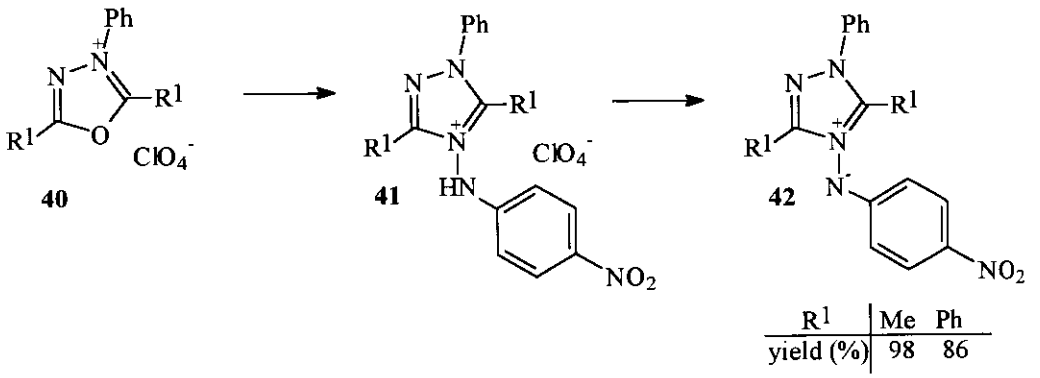
The synthesis of *N*-sulfonyl-1,2,4-triazolium derivatives (**38**) is only possible by means of path A from **32**, to avoid ring-opening reactions synthesis of **33** is carried out in non protonic solvents like nitromethane or mixtures of dioxane/pyridine in good yields (Scheme 14).[49] Sulfonamides (**33**) are easily converted into 1-alkyl-1,2,4-triazolium salts (**36**) by methyl- or benzylhalogenides, deprotonation under use of sodium hydroxide gives sulfonated azomethine imines (**38**). In mass spectra of **38** primary the cleavage of the exocyclic N-N bond takes place.

Scheme 14



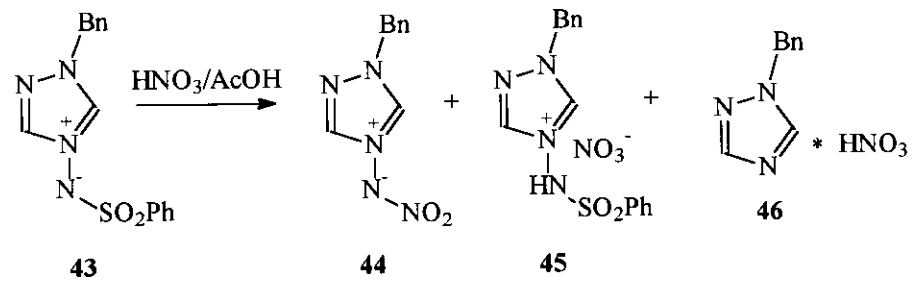
The stable bright-orange N-*p*-nitrophenyl-1,2,4-triazolium imides (**42**) have been prepared by deprotonation of perchlorates (**41**), which can also be prepared by conversion of 1,3,4-oxadiazolium salts (**40**) with arylhydrazines (Scheme 15).[50a]

Scheme 15



When nitrated by means of nitric acid in the mixture acetic acid /acetic anhydride compound (**43**) gives rise to nitro azolium imide (**44**) with yields of 45-60%. As the main by-products salt (**45**) and compound (**46**) are correspondingly formed owing to protonation of starting **43** and deamination of imide (**44**) (Scheme 16).[52]

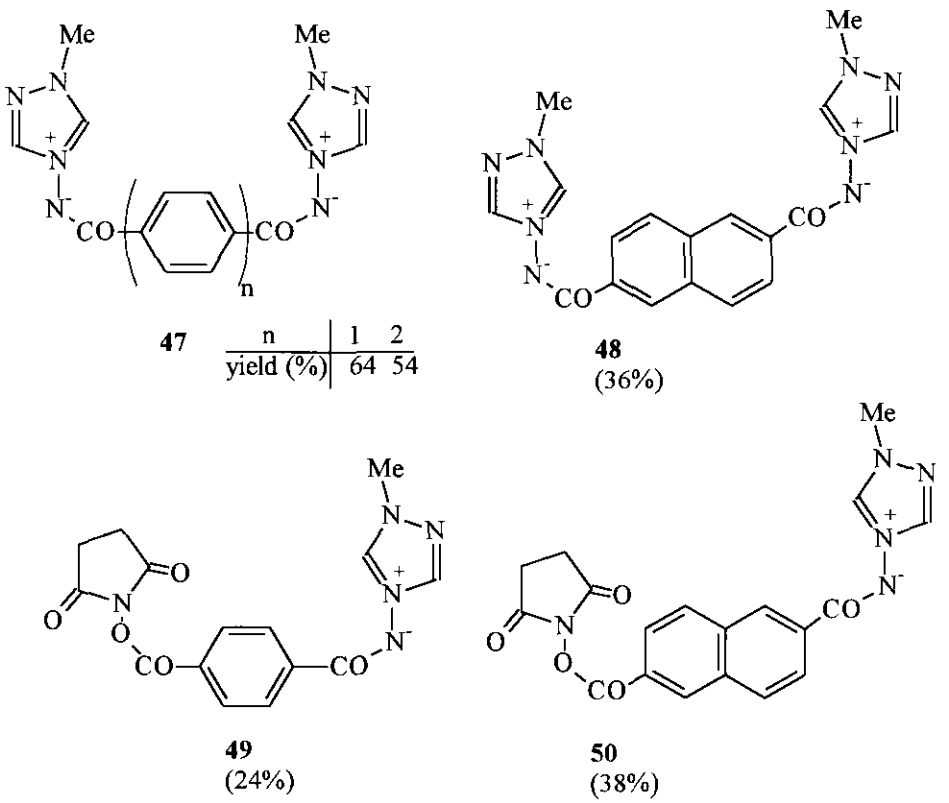
Scheme 16



The preparation of bifunctional and long-wavelength UV-absorbing reagents (**47-50**) which incorporate ylides as potential aroylnitrene precursors starts similary with a bis-acyl chloride and then deprotonation of the unisolated bis-tosylate salt with $NaHCO_3$ (Scheme 17).[56,57]

Only for the case of biphenyl-containing triazolium imides (**47**) was the strategy successful, a naphthyl group as the absorbing chromophore was unreactive; benzannulation of the nitrogen heterocycle inhibits the formation of nitrene.[57]

Scheme 17



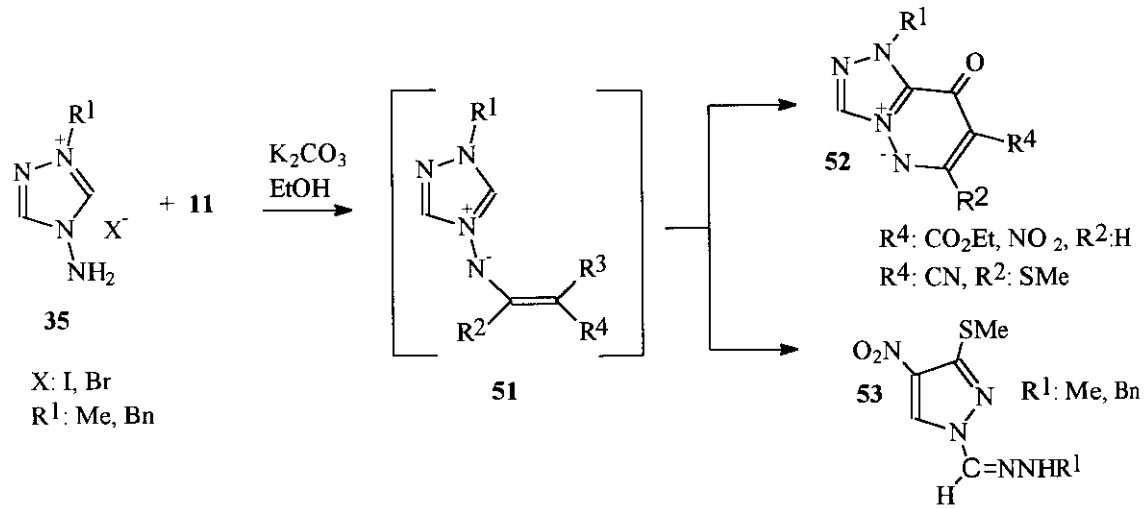
The photochemistry of substituted 1,2,4-triazolium imides (**39**) was investigated to judge their capacity to give aroylnitrenes and their suitability for use in photolabeling and photo-cross-linking experiments.[53-57]

It was found, that *N*-benzoyl imides (**39**) are stable indefinitely in aqueous solution and that their irradiation with UV gives benzoylnitrenes in excellent yield.[56] The proposal of mechanistic investigations is that benzoylnitrene is a singlet in its ground state.

The electrochemical reduction of salts (**37**) is investigated by voltammetric methods and potentiostatic electrolyses, the corresponding *N*-imides are formed.[58]

The reaction of salts (**35**) with polarized olefins (**11**) (R^3=COOMe) and K_2CO_3 in EtOH or DMSO directly yielded the back-donated 1,6-cyclization products, mesomeric betaines (**52**) *via* *N*-vinylimino ylides (**51**),[59] while the reaction of the salts (**35**) with a polarized olefin (**11**) (R^2=SMe, R^3=H, R^4=NO_2) gave the 1,5-dipolar cyclization products, pyrazoles (**53**) and for R^3=SO_2Ph, R^4=CN 1,2,4-triazolo[4,3-*b*]pyrazoles.[59] Analogs of **52** are formed by reaction of **35** with β-keto esters (Scheme 18).[60,61]

Scheme 18

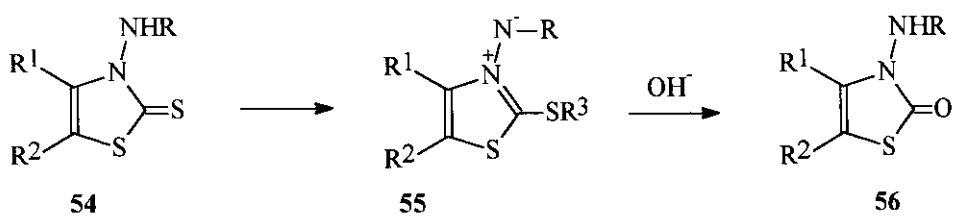


Inhibitory potential of salts (**37**) and imides (**39**) towards serine and aspartic proteases has been examined.[62,63] The acid-basic behaviour of 4-acylamino-*4H*-1,2,4-triazoles and of related structures (**37**,**39**) (R^1: CH_2COOH, R: Bn) and 3-thiones has been compared.[64]

II.5. *1,3-Thiazolium-3- imides*

This paragraph is concerned with the preparation and reactions of 1,3-thiazolium-3-imides.[65-72] *S*-Alkylation of 1,3-thiazolium-2-thiones (**54**) by means of methyl iodide or 3-ethyloxonium tetrafluoroborate gives rise to persistent 1,3-thiazolium imides (**55**), which on working up with diluted bases yield heterocycle (**56**). (Scheme 19).[65]

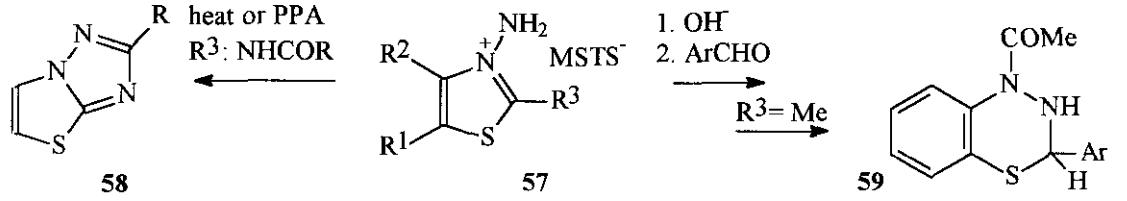
Scheme 19



R1	R2	R	R3	yield (%)
H	Ph	Tos	Me	72
H	Ph	Tos	Et	92
H	Ph	PhCO	Et	55
Me	Me	Ph	Me	not isolated

3-Aminobenzothiazolium mesitylsulfonates (**57**) (R^3= Me) react by treatment with base *via* instable 1,3-triazolium-3-imides with benzaldehyde under ring enlargement to 1,3,4-benzothiadiazines (**59**).[66] Intramolecular condensation leads to bridgehead-nitrogen heteropentalenes (**58**), when **57** (R^3=NHCOR) is heated above the melting point, or preferably, heated in PPA (Scheme 20).[67,68]

Scheme 20



58 **57** **59**

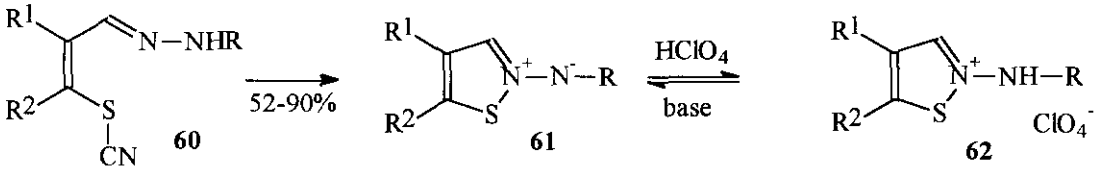
R^1, R^2: H, $(CH=CH)_2$

R^3: Me or NHCOR; R: H, Me, Ph

II.6. *Isothiazolium-2-imides*

The intramolecular cyclocondensation strategy has been expoited to construct isothiazolium-2-imides (**61**) and (**65**) depicted in Schemes 21 and 22.[73-79] The heterocyclization of 4-thiocyanato-1-aza-1,3-dienes (**60**) with various substituents R^1, R^2 and acceptor-substituted R, which were prepared from aliphatic and alicyclic β-thiocyanato vinylaldehydes with benzenesulfonyl- and benzhydrazides, yield in ethanol in all cases crystalline stable isothiazolium-2-benzoyl and phenylsulfonyl imides (**61**) as pointed out by Schulze *et al.* (Scheme 21).[74-77]

Scheme 21



60 **61** **62**

R^1	R^2
Me	Me
Ph	Me
Me	Ph
$(CH_2)_4$	

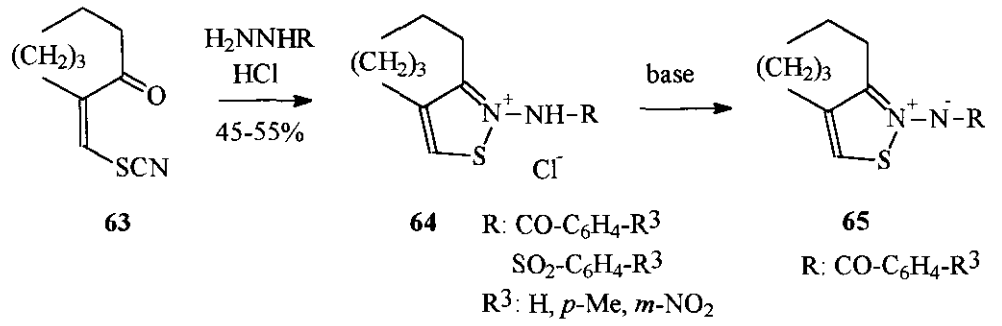
R: R^3-C_6H_4-CO,[74,75] R^3-C_6H_4-SO_2,[74,77]

R^3: H, *p*-Me, *p*-OMe, 2,4,6-$(Me)_3$
o-NO_2, *m*-NO_2, *p*-NO_2

An additional example, illustrated in Scheme 22, is particularly noteworthy, in which we have found that Z-2-thiocyanatomethylenecycloheptanone (**63**) reacts with benzhydrazides or benzenesulfonyl hydrazides

with an equimolar amount of hydrogen chloride to give the salts (**64**), only out of benzoylamide substituted salts (**64**) in reaction with a base stable *N*-benzoylimides (**65**) are yielded.[73,75]

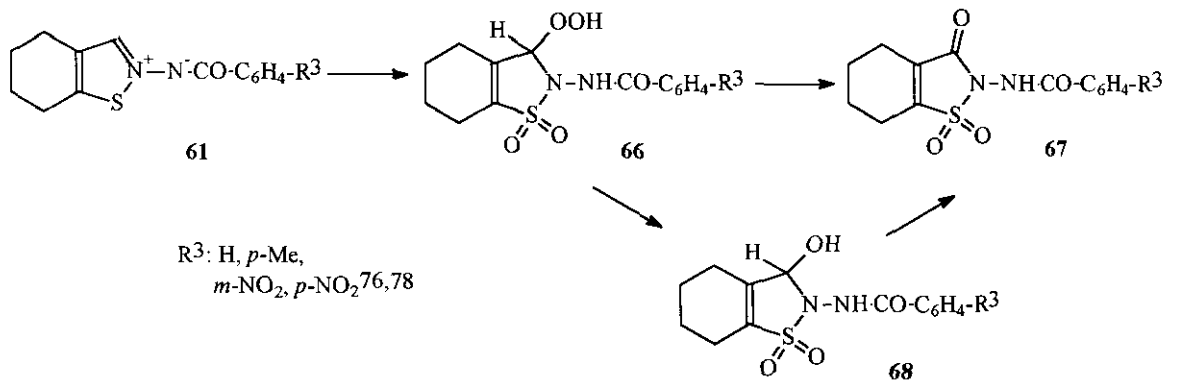
Scheme 22



63 **64** R: $CO\text{-}C_6H_4\text{-}R^3$, $SO_2\text{-}C_6H_4\text{-}R^3$; R^3: H, *p*-Me, *m*-NO_2 **65** R: $CO\text{-}C_6H_4\text{-}R^3$

Whereas the oxidation of azolium imides have been reported only by N-N bond cleavage or synthesis of tetrazenes,[4] we found surprisingly, as a general trend of oxidation of bicyclic *N*-benzoylimides (**61**) with hydrogen peroxide (30%) the formation of stable 3-hydroperoxysultams (Scheme 23),[76,78] see also.[79] The reduction of **66** proceeds to 3-hydroxysultams (**68**). Furthermore, an efficient synthetic route to 2-benzoylaminoisothiazol-3(*2H*)-one 1,1-dioxides (**67**), which are dienophiles, has been found.[78]

Scheme 23

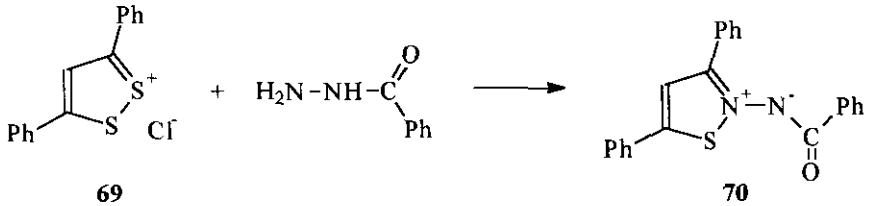


61 **66** **67** **68**

R^3: H, *p*-Me, *m*-NO_2, *p*-NO_2[76,78]

An additional synthetic approach to isothiazolium imides out of 1,2-dithiolium salt (**69**) to give the stable 3,5-disubstituted imide (**70**) is described (Scheme 24).[80]

Scheme 24



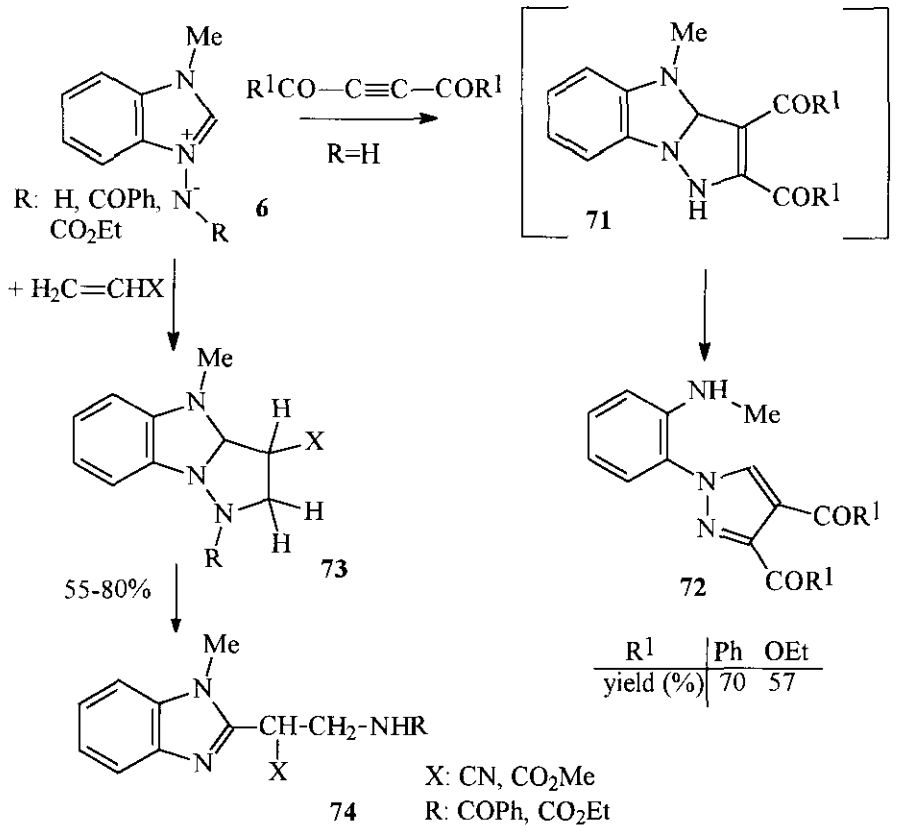
69 **70**

II.7. *1,3-Dipolar Cycloaddition*

A typical reaction of five-membered heteroaromatic *N*-imides involving the structural element of an azomethine imine is a sequence of 1,3-dipolar cycloaddition-rearrangement reactions. The cycloaddition of a variety of activated alkenes and alkynes to the azolium imides yields fused di- and tetrahydropyrazoles, respectively. Such primary cycloadducts usually undergo further tandem reactions to achieve stabilization in various ways, e.g. aromatization, hydrogen transfer, rearomatization by rearrangement and by N-N bond cleavage.[4,5,8] Kinetic and mechanistic investigation are described in a recent publication.[43]

1,3-Dipolar cycloadditions of 1-methylbenzimidazolium-3-imides (**6**) (R=H) with electron-deficient dipolarophiles give ring-opened pyrazole derivatives (**72**) *via* unisolatable cycloadducts (**71**),[81a] by contrast, the reaction of (**6**) (R=COPh) with methyl acrylate and acrylonitrile result in the N-N bond cleavage of the primary adduct to regenerate benzimidazole ring system (**74**). The intermediates (**71**) were, in fact, isolated at lower temperatures and shorter reaction times. Reaction of **6** with methyl propiolate proceeds faster then with olefins (Scheme 25).[81b]

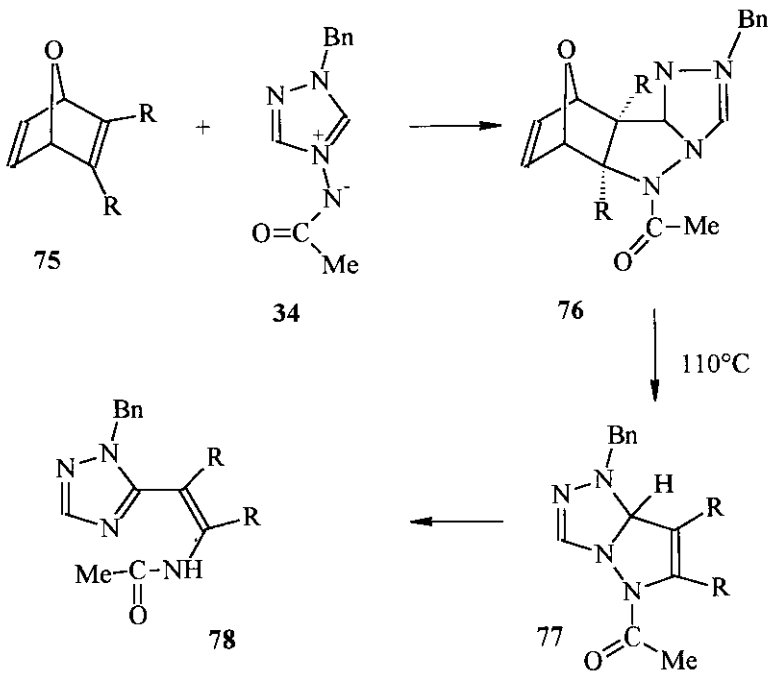
Scheme 25



Similar behavior was observed for the cycloadducts obtained from 1,2,4-triazolium-4-imides (**39**) and propiolic esters. Only acyclic products could be isolated in this case.[50b]

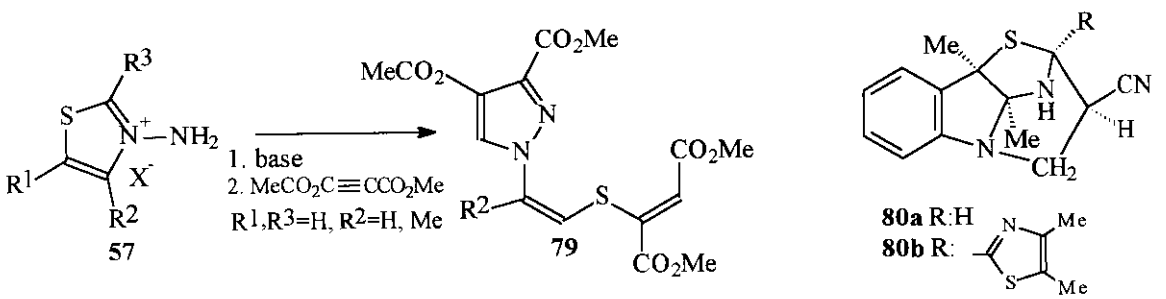
N-Acetylimide (**34**) afforded a 1:1 cycloadduct (**76**) at the deactivated double bond at room temperature, upon thermolysis at 110°C *via* an allowed cycloreversion to 77 the enamine (**78**) is formed (Scheme 26).[83]

Scheme 26



In the reaction of 1,3-thiazolium derivatives (**57**) with dipolarophiles the initially formed product further reacts with dimethyl acetylenedicarboxylate to give also pyrazol derivatives (**79**) (Scheme 27).[69,70]

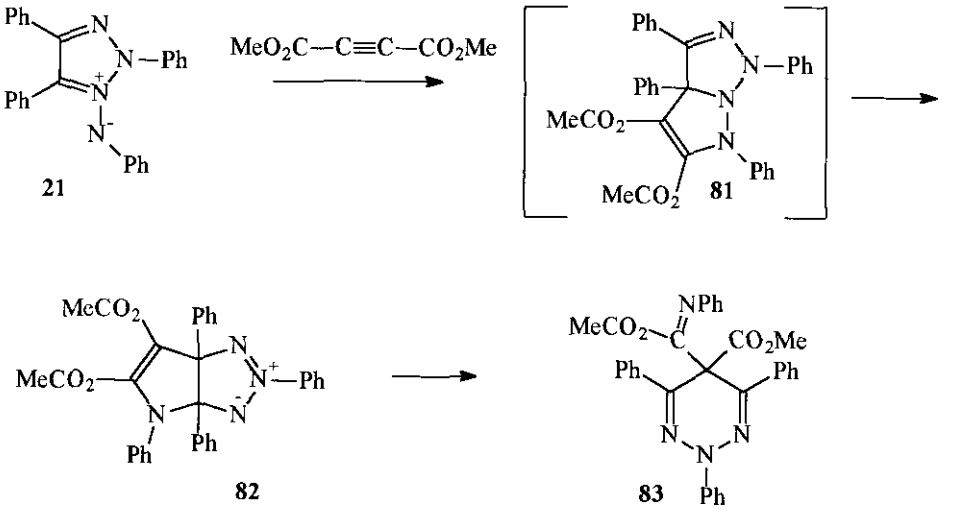
Scheme 27



4,5-Dimethylthiazolium *N*-phenylimides react with acrylonitrile in DMF to two compounds (**80a** and **80b**). For mechanism see literature.[71]

Recently, the synthetic scope of the 1,2,3-triazolium-1-imides (**21**) as 1,3-dipole has been extensively demonstrated by Butler.[8] In this report we only describe the cycloaddition of **21** with methyl acetylene dicarboxylate as an example. The primary adduct derived from **12** have the initial structure (**81**). The labile N-N bond in this species is exocyclic to the 1,2,3-triazole moiety and it undergoes in situ 1,4-electrocyclic rearrangement to give the stable structure (**82**), a fused pyrrolidinotriazoline, which will refer to as a first generation product (Scheme 28). The following structural changes to **83** can occur by heating. With some dipolarophiles the first generation products are not stable and they progress in situ to stable second generation products. With 1,2-disubstituted ethenes the reaction is rigidly stereoselective and regioselective giving single products (Scheme 28).[8]

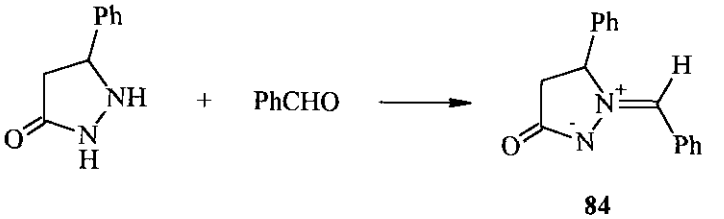
Scheme 28



III. TRIAZOLIDINIUM AND PYRAZOLIDINIUM YLIDES

It has been known that the first persistent azomethine imine (AMI) was obtained in 1955 and it was 5-membered cyclic 1-benzylidene-5-phenylpyrazolidon-3-betain (**84**) (Scheme 29).[84]

Scheme 29



In succeeding publications for the compounds of this type an alternative name was used - pyrazolidone-3-azomethine imines.[9, 10]

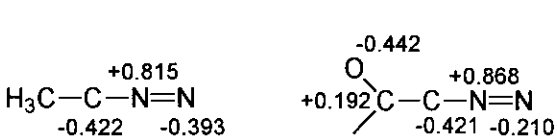
A search for a novel light sensitive compounds has stimulated a detailed study and elaboration of useful method for the preparation a wide range of the other 5-membered cyclic AMI. It was found the most powerful approach for the preparation of these AMI is reaction of aliphatic diazo compounds with 4-aryl-1,2,4-triazoline-3,5-diones.[11,85] Several tens of the new AMI were prepared using this method at the University of Kaiserslautern[86] and simultaneously at St.-Petersburg State University.[85,87-93] Some of these AMI are actually useful as the constituents for light sensitive compositions.[12]

Close inspection of the named above reaction - interaction of aliphatic diazo and azo compounds - make it possible to clarify some contradictory data in this area. Specifically, in the familiar «Comprehensive Organic Chemistry», ed. by D. Barton, 1981 is cited reaction of diazoacetic ester and triazolinedione.[94] The product of this reaction was assigned the structure of diaziridine,[95] but it is actually the oligomer of AMI.[11]

In fact, reactions that accompany intraction of aliphatic diazo compounds (ADC) with the systems bearing unsaturated N=N bond has been the subject of numerous investigations. The resulting products are on frequent occasions isomers, and could widely interconverted to one another. This complicates the interpretation of obtained results and sometimes gives rise to invalid conclusions.[11, 94,95]

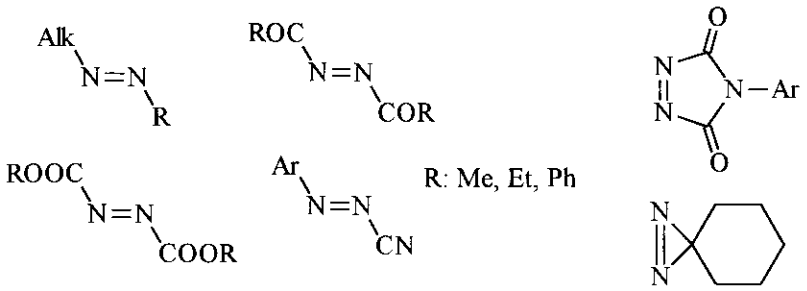
It might be assumed that in activated, that is containing electron withdrawing substituents, azo compounds N-atom is prone to interact with 1,3-dipoles that have enhanced electronic density at the C-atom of 1,3-dipolar group. Present physico-chemical investigations and quantum chemical calculations enable us to argue that in the basic state of the majority of aliphatic diazo compounds carbanion stucture prevails.[96] (Scheme 30)

Scheme 30



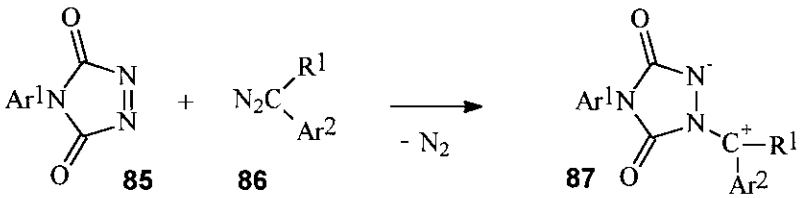
This allows *a priori* to predict that ADC are to react with azo compounds, having an activated N=N bond. And actually diazo compounds of various types - diazoalkanes, diazo esters, diazo ketones, etc. with the exception of diazo diketones[11] react easily with activated azo compounds. For an activating substituents at N=N bond could be carbonyl and ester groups, cyano and perfluoro substituents. Unsubstituted azo compounds, even with N=N bond in strained cycle, do not react with ADC in normal conditions at all (Scheme 31).[11]

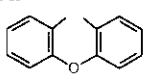
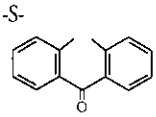
Scheme 31



In spite of the fact, that original products of the reaction are AMI (**87**), their isolation as the stable compounds is managed to perform only when used aryl substituted diazo compounds (**86**), or better still, with polyaryl nuclei. In this case the resulting new 1,3-dipole (**87**) has possbility for proficient charge delocalization, which stabilizes this species. Using this approach we synthesized a great many of persistent AMI (Scheme 32). [11, 85,88,90]

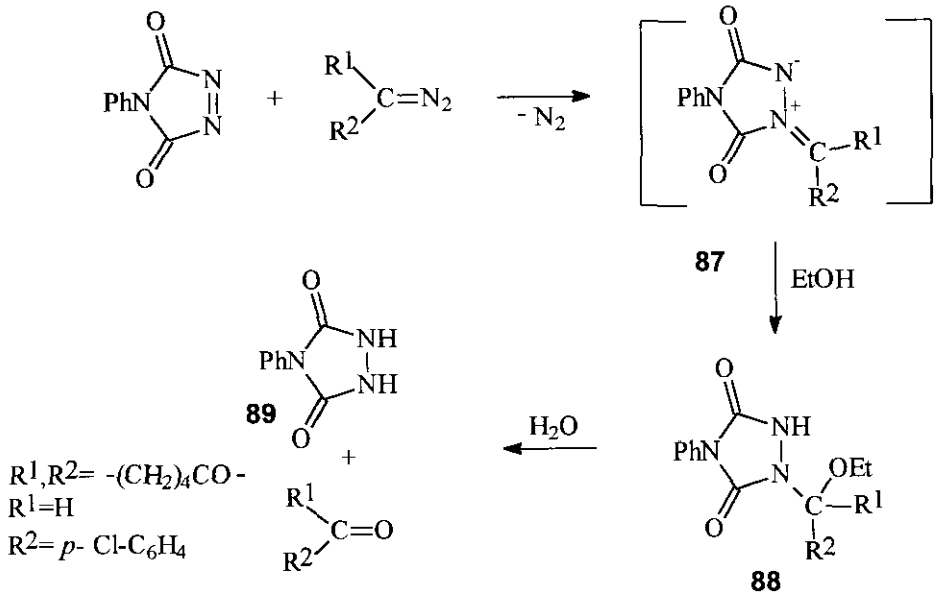
Scheme 32



	Ar¹	R¹	Ar²: C_6H_4-R²	yield (%)	mp °C
a	Ph	H	H	70	152-154
b	Ph	H	*p*-NO_2	75	118-120
c	Ph	H	*p*-CN	72	114-116
d	Ph	H	*p*-F	65	115-116
e	Ph	H	*o*-F	68	143-145
f	Ph	H	*p*-Me	75	101-102
g	Ph	H	*p*-NMe_2	63	195-196
h	Ph	H	*p*-NEt_2	67	201-202
i	Ph	Ph	H	97	126
j	Ph	Ph	*p*-NO_2	51	106-107
k	Ph	Ph	*p*-F	97	147-148
l	Ph	Ph	*p*-CH_2-CN	88	127-130
m	Ph	Ph	*p*-OMe	87	125-126
n	Ph	Ph	*p*-NMe_2	85	185-187
o	Ph	*m*-NO_2-C_6H_4	*m*-NO_2	65	110-112
p	Ph	Ph	Ph	90	151-152
q	Ph	Ph	Naphth.	63	145-147
r	Ph	Ph	2-Thioph.	76	157-158
s	Ph			65	137-139
t	Ph	-S-		61	141-142
u	Ph			71	154-155
v	*p*-NO_2-C_6H_4	Ph	H	67	136-137
w	*o*-CH_3-C_6H_4	Ph	H	90	133-134
x	*p*-OCH_3-C_6H_4	Ph	H	94	147-149

When operating with monoaryldiazomethanes, to obtain relevant AMI in substance much care must be taken to follow the reaction conditions, purity of the solvents, etc.[91] In the case when AMI (**87**) is not obtained in substance, its intermediate formation can be verified using EtOH as reaction solvent. Under this conditions AMI is turned to highly reactive so called aminal (**88**), that hydrolyzed easily to urazole (**89**) and the appropriate ketone. It should be emphasized here hydrolysis of aminals is normally realized in some minutes, wheras it takes a few days to hydrolyze associated AMI at the same conditions (Scheme 33).

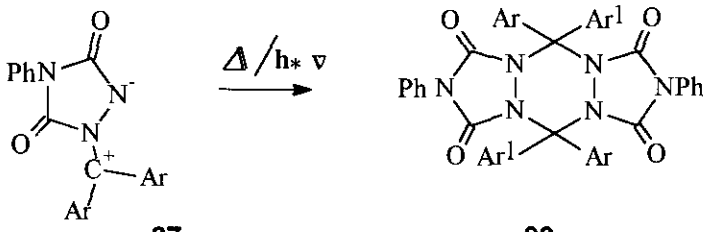
Scheme 33



We replicate Izydore's and McLeane's[95] experiment with diazoacetic ester and PTAD, that according to these authors gave rise to the formation of diaziridine. It was found that the oligomer is formed under the test conditions but no 3-membered heterocycle. Di- and oligomerization products were isolated as well with ADC of the other types: with diazoalkanes, a few monoaryldiazomethanes, some diazo ketones, specifically, with diazooxocyclanes and diazooxotetrahydrofurans.[11, 87,88]

Reasoning from the spectroscopic data and literature parallels[114] it may be concluded, that azomethine imine fragment takes place in polymerization process. In dimerization process [3+3] «head to tail» addition realizes. In many instances we specifically synthesized the dimers (**90**) of this kind from the stable, isolated in substance AMI (Scheme 34).[11, 97-99]

Scheme 34

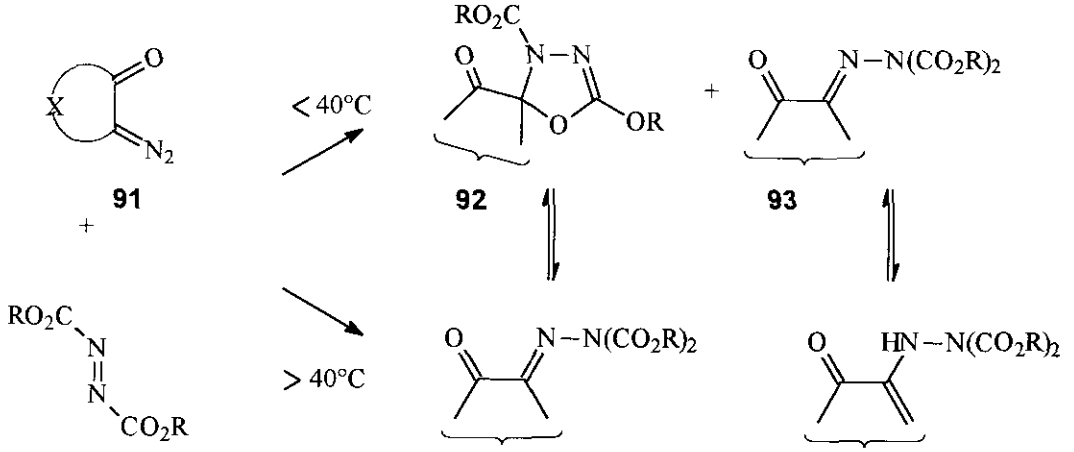


87 **90**

Thus, at normal conditions of reaction performing, in ether at room temperature, interaction of *cis*-azo compounds with ADC containing aryl or other structural fragments which are capable to stabilize the arising 1,3-dipole, stable AMI are usually emitted from reaction mixture. At the same time diazoalkanes, diazo ketones, and diazo esters, which have structurally no way for effective stabilization of charges in 1,3-dipolar AMI, give rise to dimers or oligomers of originally formed azomethine imine.

It is well known interaction of alicyclic diazo compounds (**91**) with *trans*-azo compounds does not yield AMI and in this process oxadiazolines (**92**) and/or hydrazones (**93**) are formed. Occasionally these compounds interconvert to one another.[97] The controlling factor in this transformation has the temperature of the process: it was found bellow 40°C oxadiazolines (**92**) are mainly generated, but at the higher temperatures exclusively di(carbalkoxy)hydrazones (**93**) are formed. The yields in both cases are almost quantitative (Scheme 35).[97,100]

Scheme 35

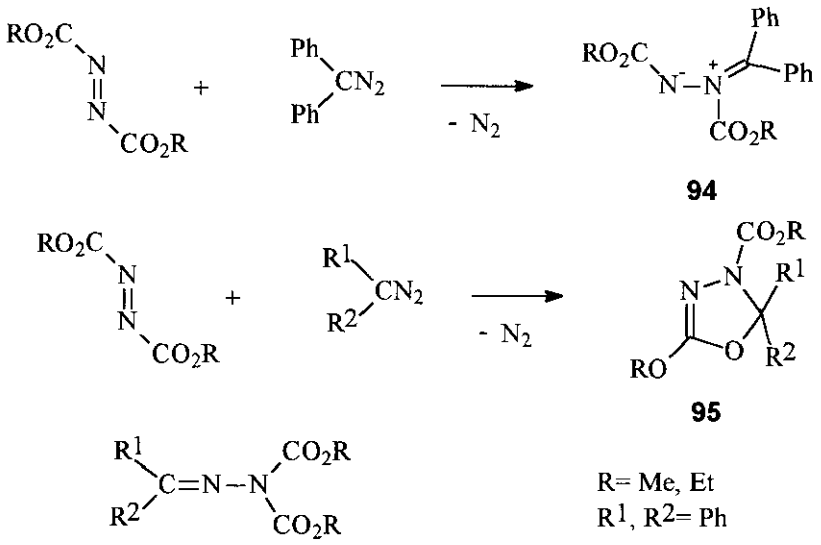


X: $(CH_2)_4$; $(CH_2)_3$; $C(Me)_2OC(Me)_2$

standing of oxadiazolines, but it is strongly accelerated by the means of heating. These results were obtained by the examples of diazooxocyclanes and 2,2,4,4-tetraalkyl substituted diazooxotetrahydrofurans.[100]

Our conclusion that interaction of *trans*-azo compounds and ADC generally gives rise to two types of reaction products-oxadiazolines and hydrazones, and not to AMI were in contradiction with earlier results of Bettinetti.[101] These authors mention in their work that interaction of *trans*-azo ester and diphenyldiazomethane yields colored appropriate AMI (**94**) (Scheme 36).

Scheme 36



We replicated their experiment, but unfortunately were unable to obtain even traces of AMI, but only colourless oxadiazoline (**95**) with excellent yield. Similar results were obtained with other aryldiazo methanes, including diazothioxantene.[8,98]

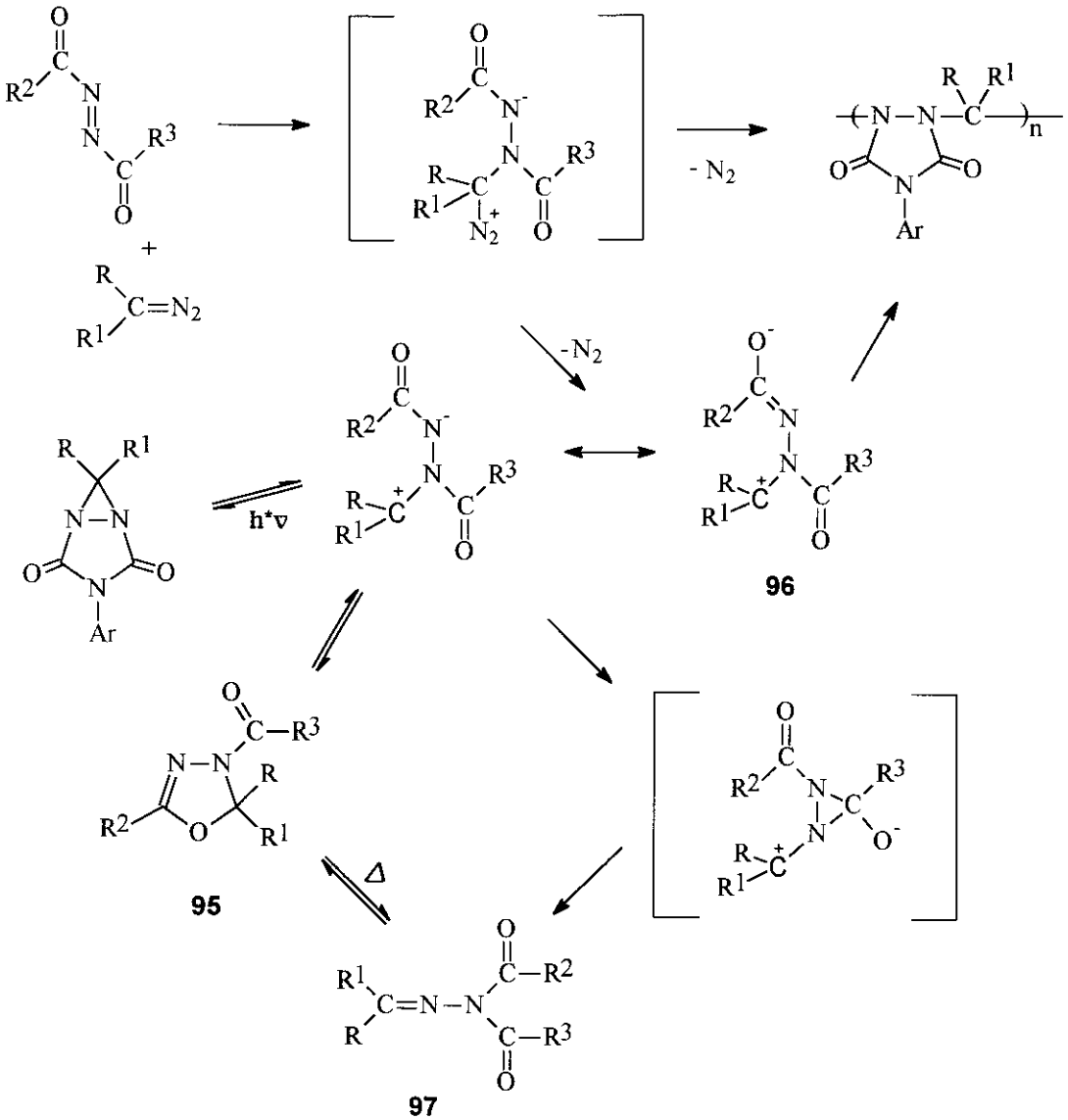
Nevertheless, it is not currently possible to exclude the occurrence in solution of fast equilibrium between AMI (**94**) and oxadiazolines (**95**).

Summarizing, it is reasonably safe to suggest that at the first stage of reactions under review readily polarized N=N bond of azo compounds is attacked by nucleophilic C-atom of diazo group with subsequent elimination of dinitrogen of diazo compound. Taking into account investigated ADC are rather stable at the conditions studied it is valid to suggest intermediable formation of tetrazoline or diazonium structure, but no carbene (Scheme 37).[94]

Elimination of dinitrogen yields new 1,3-dipole - AMI (**96**) and plausible stabilization pathway of these species are represented on the general Scheme 37. At its centre AMI is depicted in the form that shows a

tendency for closure to oxadiazoline cycle (**95**). On the other hand it is also readily apparent from the picture the way for hydrazones formation (**97**).

Scheme 37



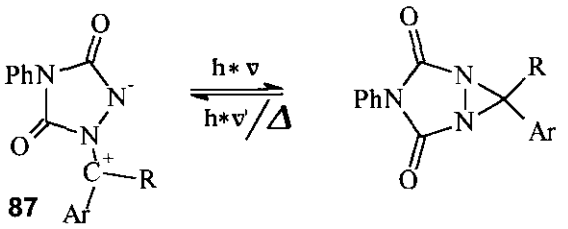
Clearly AMI can be obtained in substance when ring closure to oxadiazoline structure in this species is ruled out. This is possible in two cases only:- firstly, when starting azocompound does not have carbonyl group in substituents at N=N fragment on the molecule; in fact, R. Huisgen *et al.* [102] obtained stable open chain AMI when used azocyanides in reaction with ADC.

-secondly, ring closure to oxadiazolines is actually impossible by stereochemical reasons, if starting azo compound has *cis*-fixed configuration.

And numerous stable AMI, prepared by Russian[11,85,98] and German[86] chemists, are the best experimental verification of this speculations.

It seems, diaziridines in direct reaction of azo and diazo compounds were not obtained yet. We have established, however, 3-membered ring closure of AMI (**87**) can be realized in their excited state, upon UV irradiation of AMI, prepared from PTAD and monoaryldiazomethanes (Scheme 38).[13]

Scheme 38



87

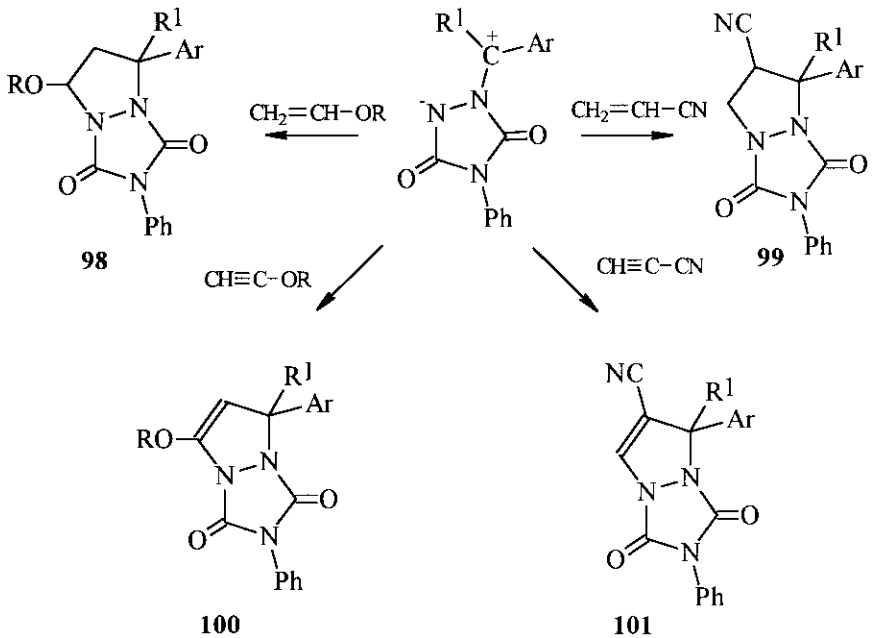
Photochemical cyclization with the formation of diaziridines has also received much study in Humboldt University at the example of pyrazolidone-3-azomethine imines. These investigations included careful spectroscopic studies and X-Ray analysis of diaziridines obtained.[9, 10, 14]

Similar photochemical reactions have been performed by K. Burger *et al.* with the cyclic AMI, stabilized by *trifluormethyl substituents.*[103-105] However as the final product in these reactions proved to be a 1,3-diazobicyclo[3.1.0]hexene. The occurrence of this compound are attributable to intermediate origination of the associated diaziridine .

The most distinctive chemical feature of AMI as 1,3-dipole is their ability to react with unsaturated compounds with the addition to carbon-carbon double and triple bonds. Using dipolarophiles with electron withdrawing substituents at multiple bonds, we obtained isomeric cycloadducts (**98-101**) having β-electronegative substituents to *N*-atom of heterocycle. Utilizing in this reaction of dipolarophiles with electron releasing groups at multiple bond yields heterocycles bearing electron releasing substituents in α-position to nitrogen atom of the cycle (Scheme 39).[106,107]

These results are indirect evidence in favour of the implication, that in resonance hybride of being considered AMI 1,3-dipole (**87**) a limited structure with enhanced electronic density on *N*-atom rather than on C-atom contributes significantly, that is AMI can be conceived of as reversed 1,3-dipoles with respect to aliphatic diazo compounds.[11]

Scheme 39

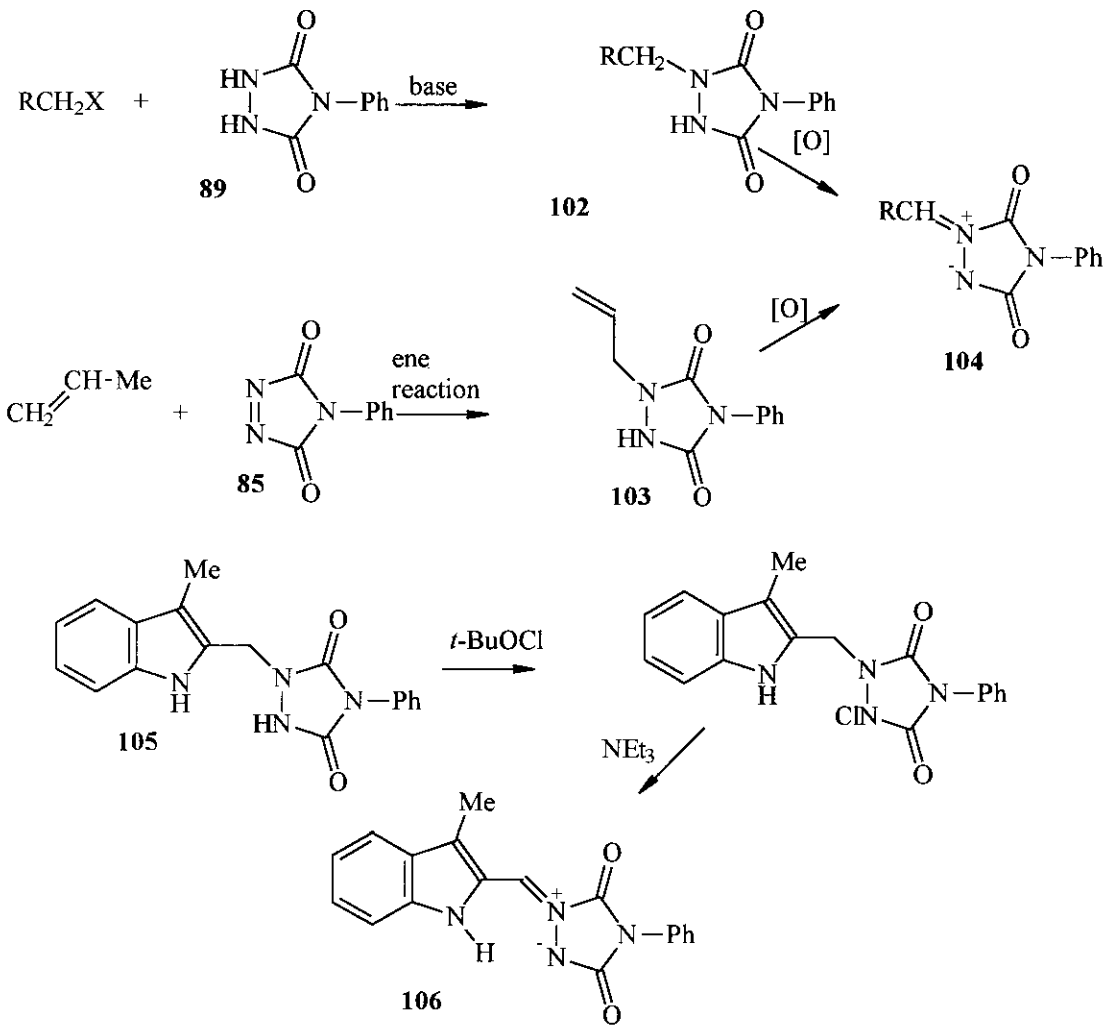


Thus, triazolindione ylides (**87**) have been isolated from the reactions of triazolinediones (**85**) with appropriately substituted diazoalkanes,[85,86,90,98] isobenzofurans,[108] acetylenes.[109] However, all of these entries to triazolinedione ylides are rather limited in scope and not of broad synthetic utility. *N*-substituted *N*-phenylurazoles (**102,103**) are readily available from simple nucleophilic substitution reactions and perhaps even more generally through the ubiquitous ene-reaction of olefins with *N*-phenyltriazoline dione (**85**), leading to isolatable (**104**) (Scheme 40).[110,111]

The ylide of *N*-phenyltriazolinedione are readily prepared when the ylide carbon atom is substituted by phenyl or 3-methylindol-2-yl groups.[110] In fact the indole-substituted ylide (**106**) is sufficiently stable to be isolated in good yield when it is formed by the oxidation of the corresponding urazole (**105**) with *tert*-butyl hypochlorite followed by dehydrohalogenation with triethylamine.

The intensive advancement of the procedure for the preparation of persistent AMI from the cyclic hydrazine derivatives (pyrazolidones) and carbonyl compounds is currently still in progress. Specifically, a fascinating application of this approach has been recently described for stereoselective synthesis of C-nucleosides:[112] the fused NH,NH-dihydropyrazole derivative was transformed with carbohydrates into chiral azomethine imine; the 1,3-dipolar cycloaddition of these to methyl acrylate afforded the nucleosides. Intramolecular AMI cycloaddition of the same type were also investigated recently.[113]

Scheme 40



A new type of highly polar 1,3-dipoles has been synthesized from their 3-oxo analogues and Lawessons reagent. We are dealing with a thiocarbonyl stabilized pyrazolidin-azomethine imines, which dipole moments are even higher than those of their 3-oxo analogues.[115]

ACKNOWLEDGEMENTS

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