INTRAMOLECULAR REACTIONS OF NITRILIMINES AS A FRUITFUL SOURCE OF HETEROCYCLES

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Abstract- The multiform intramolecular reactivity of nitrilimines is presented in a systematic way, giving emphasis to its versatile potential in heterocyclic synthesis.

CONTENTS

I. INTRODUCTION

Fifty years ago, in the course of their studies on the pyrazole synthesis from hydrazonyl halides, Fusco and Romani[1] perceived the intermediacy of novel species isomeric with respect to the already known diazoalkanes. Later, Huisgen defined the correct nature of these labile intermediates and named them nitrilimines.[2] Direct evidence of the transient formation of nitrilimines has been acquired by UV, IR, and photoelectron spectroscopy.[3-6] The obtainment of stable nitrilimines has been recently reported.[7] Nitrilimines belong to the class of the so-called 1,3-dipoles and their cycloadditions to multiple bonds are the object of a copious body of literature.[8-10]

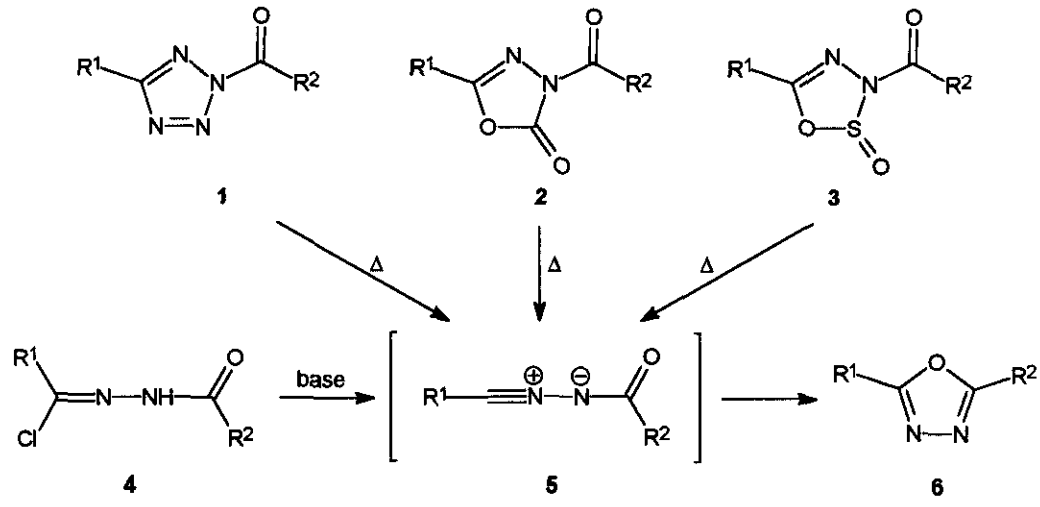
Suitably functionalized nitrilimines are susceptible to an interesting variety of intramolecular reactions, some of which lack analogy at the intermolecular level. The present paper is aimed at offering a systematic and rational survey of the multiform reactivity of nitrilimines at the intramolecular level.

II. 1,5-ELECTROCYCLIZATIONS

In line with the general behavior pattern of α,β-unsaturated 1,3-dipoles,[11,12] nitrilimines bearing a double bond at the *N*-terminus are prone towards the 1,5-electrocyclic closure depicted in the following equation:

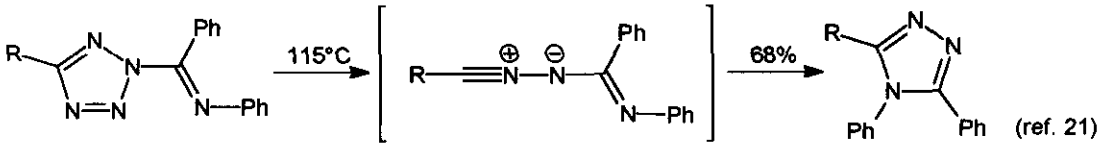
A long-known synthesis of 1,3,4-oxadiazoles (**6**) is just based on the 1,5-cyclization of *N*-carbonyl-nitrilimines (**5**), which can be generated *in situ* by *(i)* thermal extrusion of nitrogen from 2-acyltetrazoles (**1**)[13,14] *(ii)* thermal extrusion of carbon dioxide from 4-acyl-1,3,4-oxadiazol-5-ones (**2**)[15,16] *(iii)* thermal extrusion of sulfur dioxide from 3-acyl-1,2,3,4-oxathiadiazole 2-oxides (**3**)[17] *(iv)* base-induced elimination of HX from *C*-halo-*N*-acylhydrazones (**4**)[18-20] (Scheme I). The analogous formation of 1,3,4-thiadiazole derivatives from *N*-thiocarbonylnitrilimines is also known.[13]

Scheme I

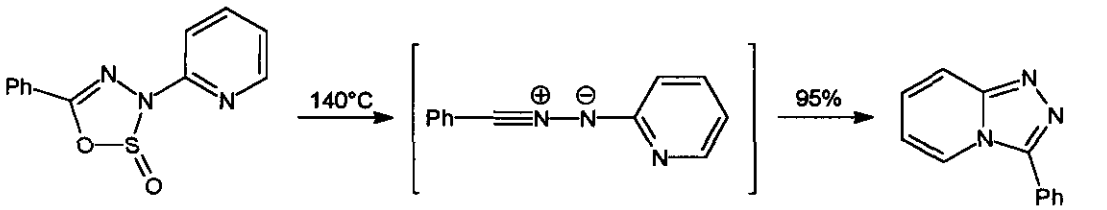


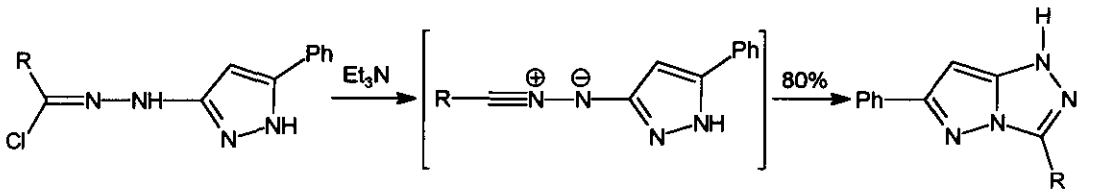
1,5-Electrocyclizations of *N*-imidoylsubstituted nitrilimines constitute a facile synthetic entry to 1,2,4-triazole derivatives.[21] Fused-ring 1,2,4-triazoles are formed whenever the imino moiety is incorporated into a heterocyclic nucleus.[22-28] Significant examples are illustrated in Scheme II.

Scheme II



R = 4-$NO_2C_6H_4$

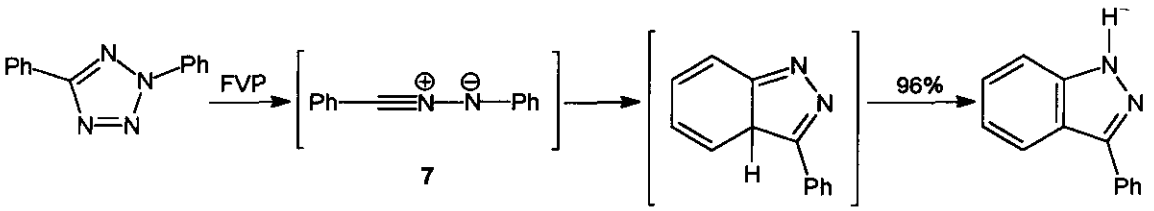




R = COMe

Under flash vacuum pyrolysis conditions, the first-formed *N*-arylnitrilimines (**7**) evolve to indazoles (**8**) (Scheme III).[29] This reaction, which is often interpreted in terms of azocarbene-like reactivity, correctly belongs to the 1,5-electrocyclic changes of 6π-electron systems.

Scheme III



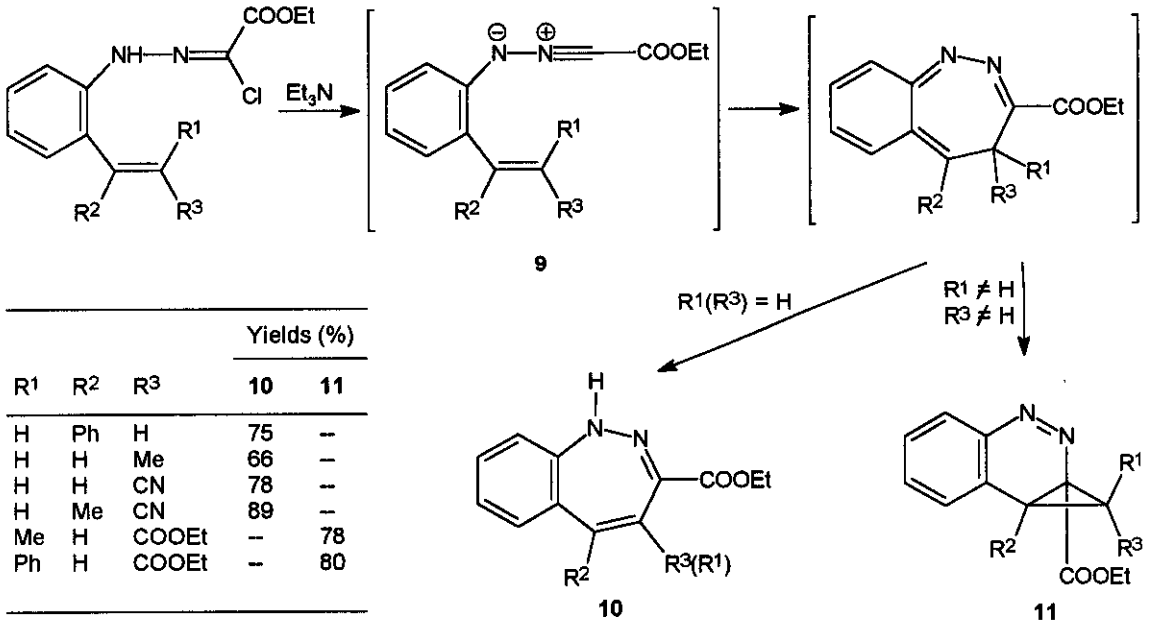
7 **8**

III. 1,7-ELECTROCYCLIZATIONS

Nitrilimines having both α,β- and β,γ- unsaturations are in principle susceptible to 1,7-electro cyclization of the 8π-electron system. However, this process is really occurring provided that the competitive 1,5-cyclization is somewhat depressed by suitable structural factors, *e.g.* incorporation of the α,β-unsaturation into an aromatic nucleus. Actually, the *in situ* generation of *N*-(2-vinylphenyl)

substituted nitrilimines (**9**) results directly in 1*H*-1,2-benzodiazepines (**10**), whose formation is well explicable in terms of 1,7-electrocyclization followed by restoration of the aromaticity through hydrogen shift (Scheme IV).[30-33] When the latter rearrangement is precluded by the absence of hydrogen(s) in the appropriate position, cyclopropa[*c*]cinnolines (**11**) are formed as alternative products.

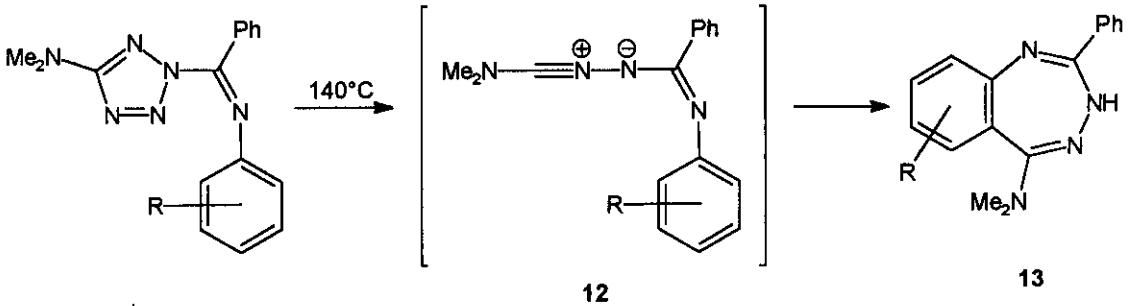
Scheme IV



			Yields (%)	
R^1	R^2	R^3	**10**	**11**
H	Ph	H	75	--
H	H	Me	66	--
H	H	CN	78	--
H	Me	CN	89	--
Me	H	COOEt	--	78
Ph	H	COOEt	--	80

The particular α,β,γ,δ-unsaturated nitrilimines (**12**) have been reported to suffer from 1,7-electrocyclization giving 1,3,4-benzotriazepines (**13**) (Scheme V).[34]

Scheme V



R	H	4-Cl	4-Me	2,4-Me_2
Yield (%)	42	73	85	68

A 1,7-electrocyclic process is reasonably involved, as the first step, in the long-known conversion of *N*-(2-nitrophenyl)substituted nitrilimines to *N*-acyloxybenzotriazoles.[14, 35-37]

IV. 1,3-DIPOLAR CYCLOADDITIONS TO CARBON-CARBON MULTIPLE BONDS

A copious literature[38-58] is available about the intramolecular nitrilimine cycloadditions to alkene and alkyne functionalities and a fascinating array of fused-ring pyrazoles have been constructed by means of this strategy. As a general trend, such reactions proceed efficiently irrespective of the fact that the chain containing the dipolarophile group is linked to the *N* or *C* terminus of the dipole. However, this is true provided that the proximity effect works to facilitate the intramolecular approach. In other words, the length and the conformational flexibility of the tether between the addends play an important role in determining the behavior of alkenyl and alkynyl substituted nitrilimines.

IV.1. Formation of Pyrazoles Annulated to a Five-membered Ring

Both *N*-functionalized[38-40] and *C*-functionalized[41,42] nitrilimines are able to undergo intramolecular cycloadditions producing pyrazoles annulated to a five-membered ring. Significant examples are given in Scheme VI. Geometric constraints due to the intramolecularity are responsible for the formation of **19**, which involves a regiochemistry opposite to that operative in intermolecular nitrilimine cycloadditions onto terminal alkenes and alkynes.[8,9] On the same grounds, one can explain other peculiar features: *(i)* the leveling of the kinetic effect of both Ar and R substituents in compound (**14**); *(ii)* the unique diastereopreference in the cyclization of **16**.

IV.2. Formation of Pyrazoles Annulated to a Six-membered Ring

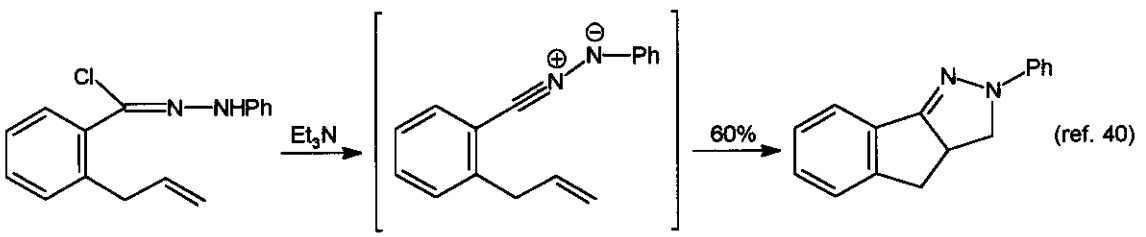
The formation of pyrazoles annulated to a six-membered ring *via* intramolecular nitrilimine cycloadditions is amply documented.[3,38,41,43-50] Scheme VII illustrates a few selected examples. Once again, one can see that geometric more than electronic factors dictate the regiochemistry of the intramolecular process.

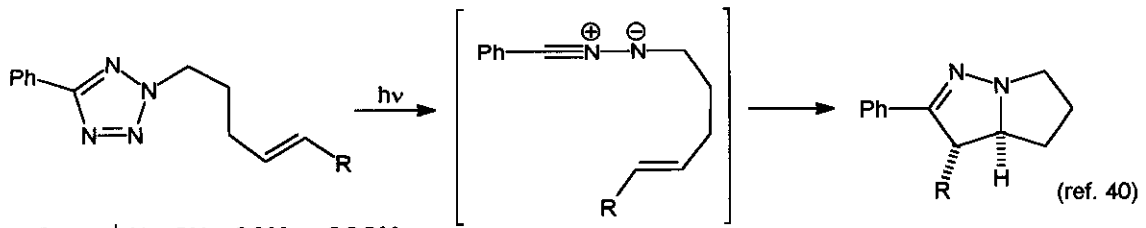
IV.3. Formation of Pyrazoles Annulated to a Seven-membered Ring

The pharmacological activity of several hetero-annulated benzodiazepines[51] has prompted a search for the synthesis of them as well as of related heterocycles by intramolecular nitrilimine cycloadditions. This strategy has been successful for the preparation of [1]benzoxazepino[5,4-*c*]pyrazoles (**20**) (Scheme VIII),[3] pyrazolo[1,5-*a*][5,1]benzoxazepines,[41,44] pyrazolo[1,5-*a*][4,1]benzoxazepines,[52-54] pyrazolo-

[1,5-*a*][1,4]benzodiazepines (**21**) (Scheme VIII),[55] and pyrazolo[1,5-*a*][4,1]benzothiazepines (**22**) (Scheme VIII).[56]

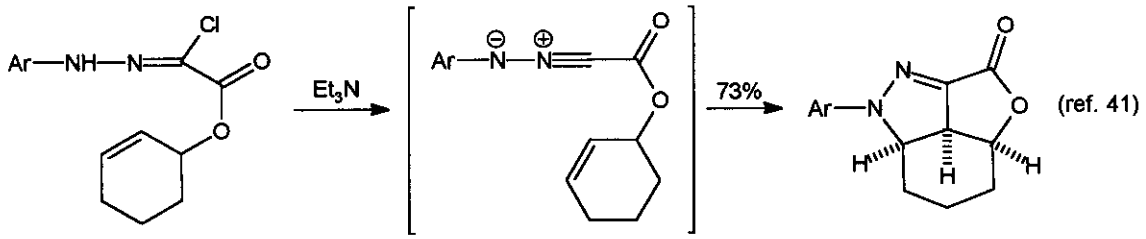
Scheme VI



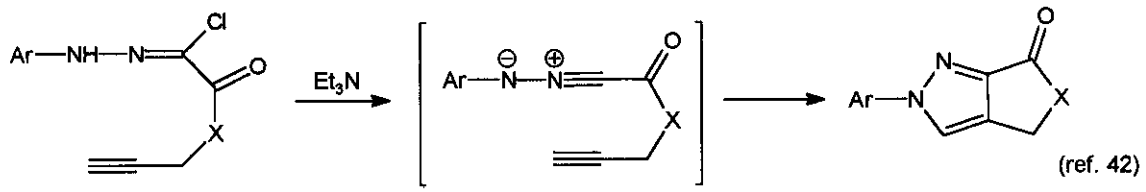


R	H	CN	COMe	COOMe
Yield (%)	90	71	48	88

14 **15**



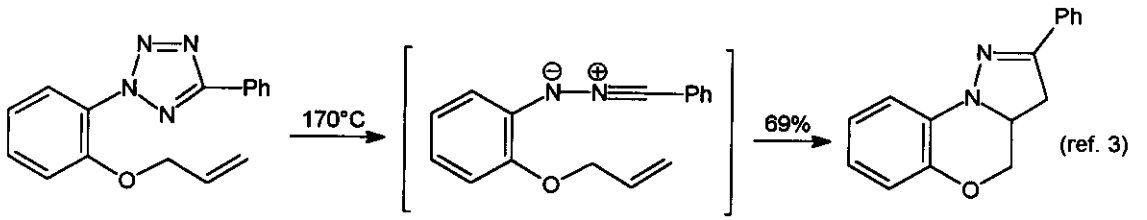
Ar = 4-ClC$_6$H$_4$ **16** **17**

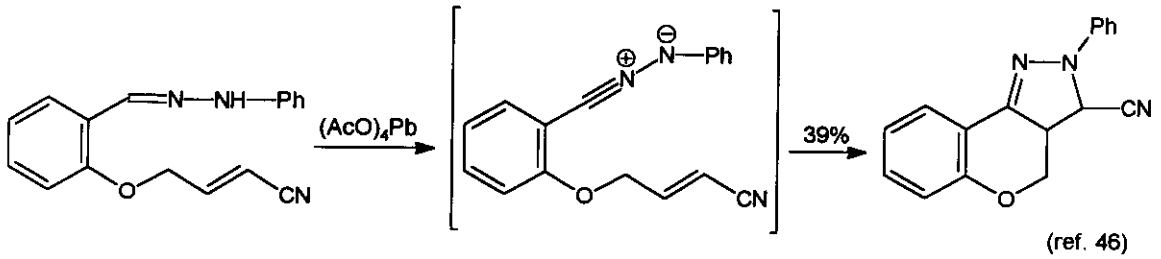


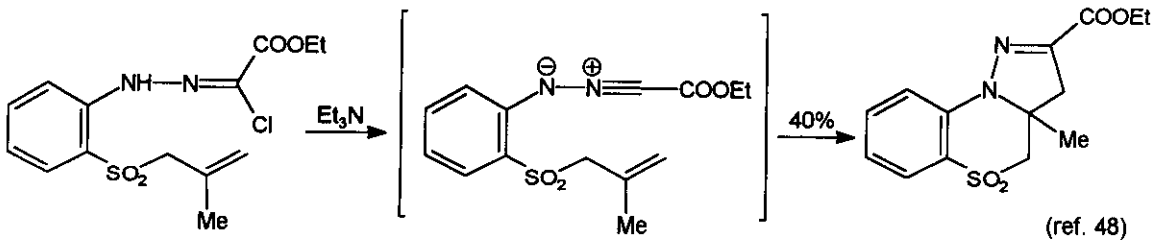
Ar = 4-ClC$_6$H$_4$ **18** **19**

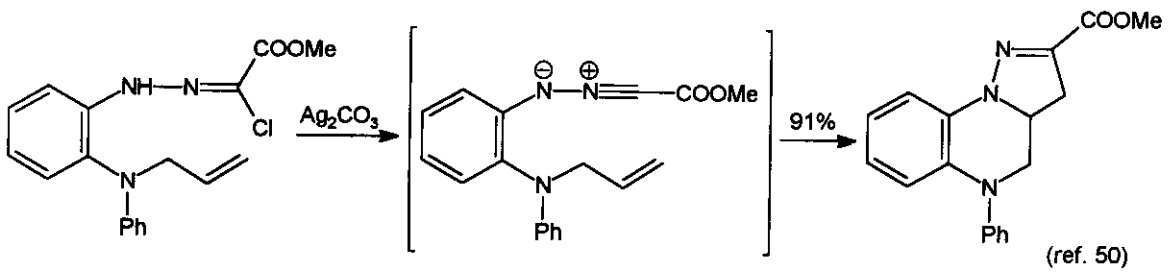
X	O	NH
Yield (%)	54	37

Scheme VII

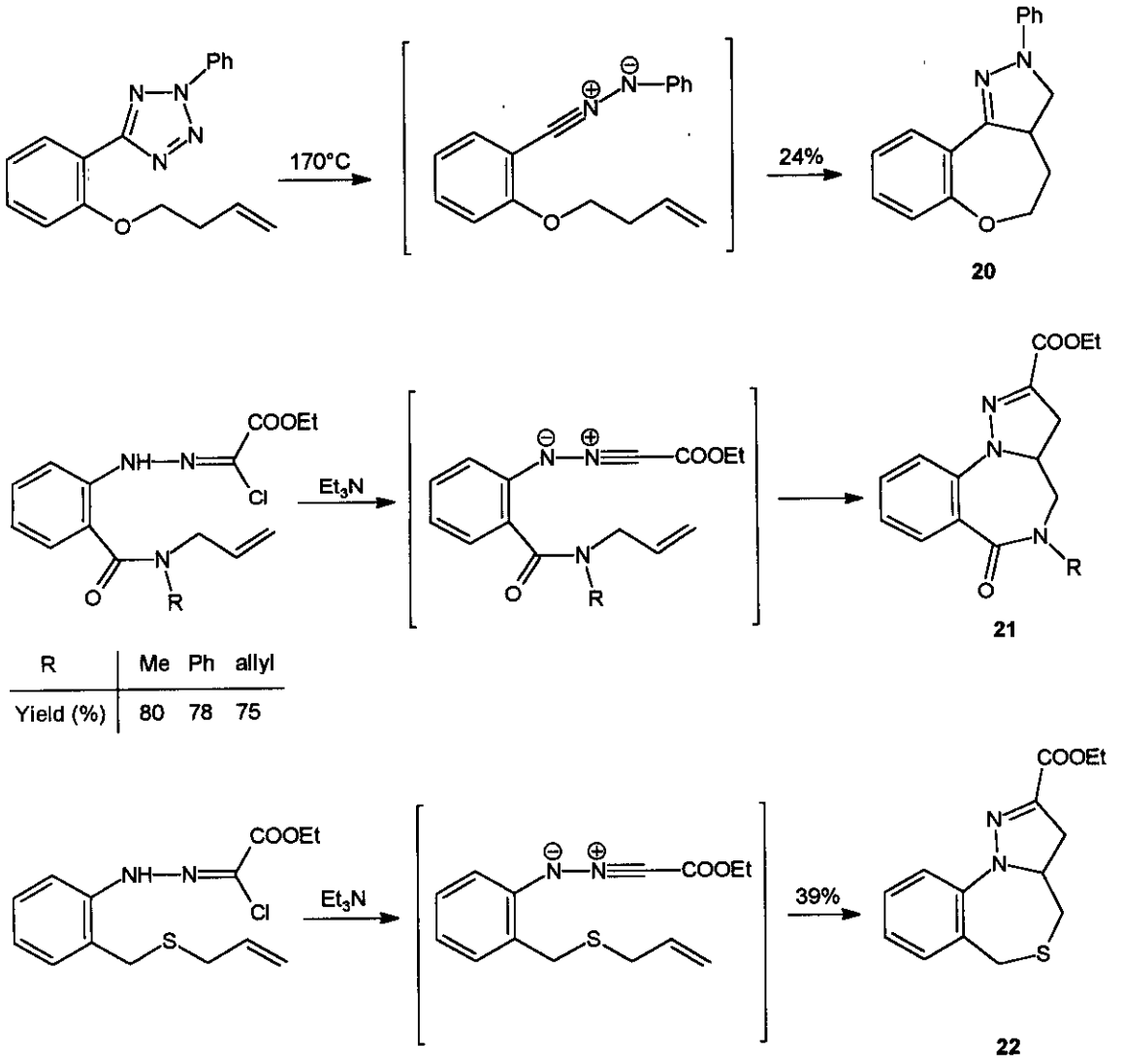

170°C
69%
Ph
(ref. 3)


(AcO)4Pb
39%
CN
(ref. 46)


Et3N
40%
COOEt
Me
(ref. 48)


Ag2CO3
91%
COOMe
Ph
(ref. 50)

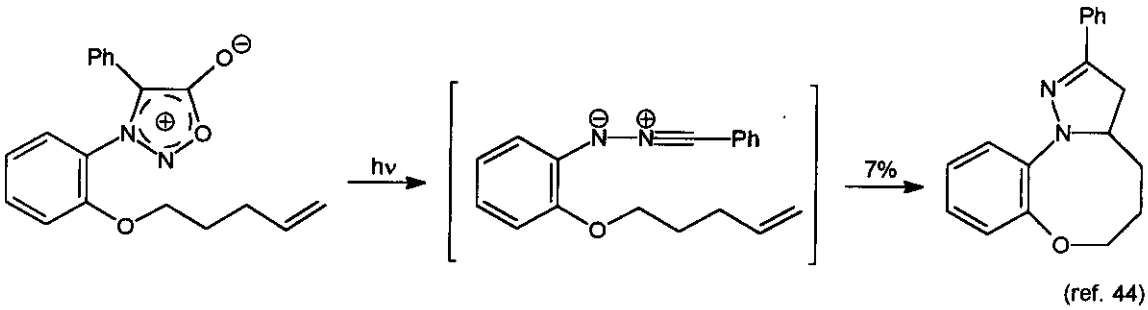
Scheme VIII



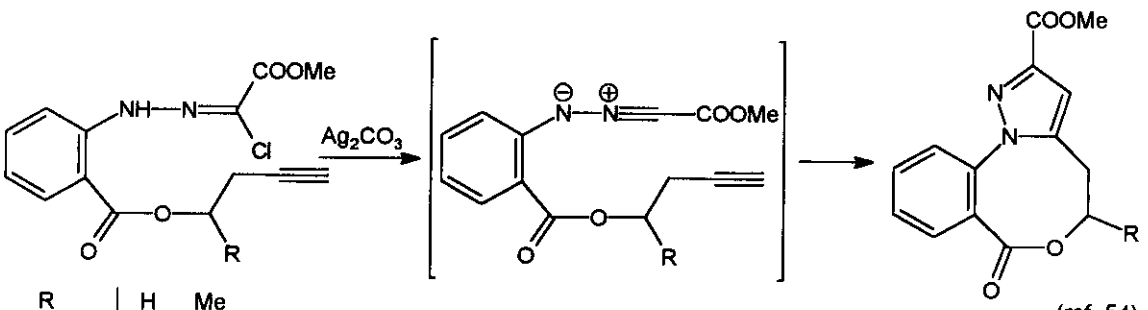
IV.4. Formation of Pyrazoles Annulated to a Medium-sized Ring

The intramolecular nitrilimine cycloaddition strategy has been exploited to construct the array of heterocyclic skeletons depicted in Scheme IX.[44,53,54,57-58] An additional example, illustrated in Scheme X, is particulary noteworthy owing to the azacrown ether nature of the products.[59] In cases where nitrilimines have been generated from hydrazonyl chlorides, silver carbonate has been found more fruitful than conventional bases such as triethylamine. It may be that, due to its insolubility in organic solvents, this salt produces a very low concentration of nitrilimine, so mimicking the high dilution conditions which are well-known to favour cyclization over polimerization of bifunctional reactants.

Scheme IX

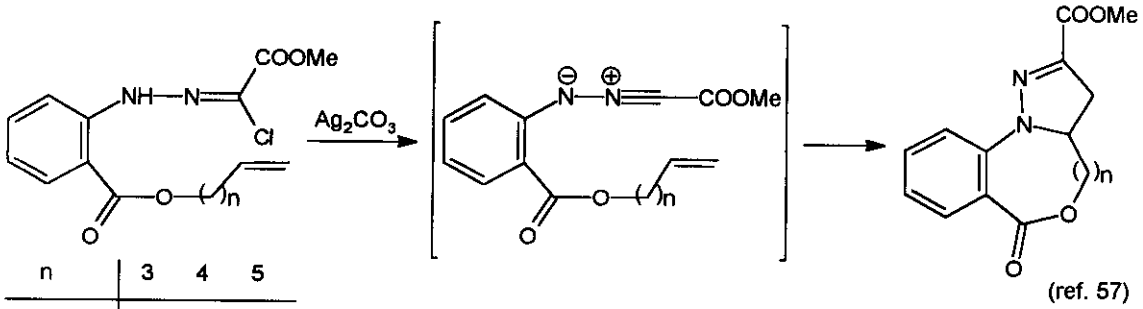


(ref. 44)



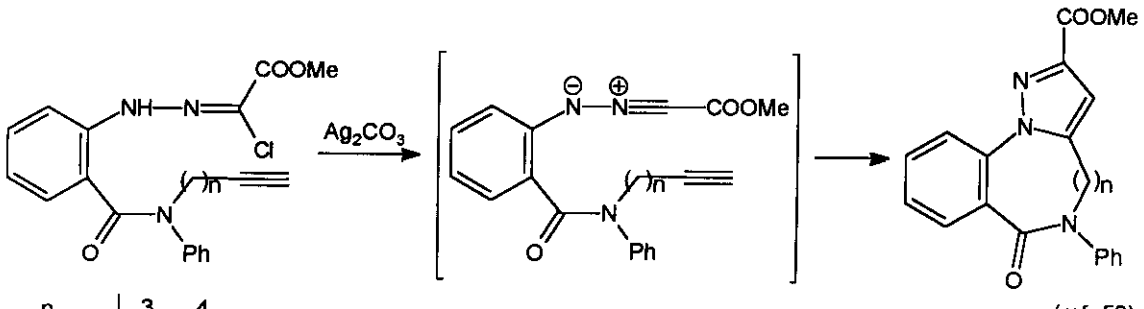
R	H	Me
Yield (%)	21	47

(ref. 54)



n	3	4	5
Yield (%)	18	37	21

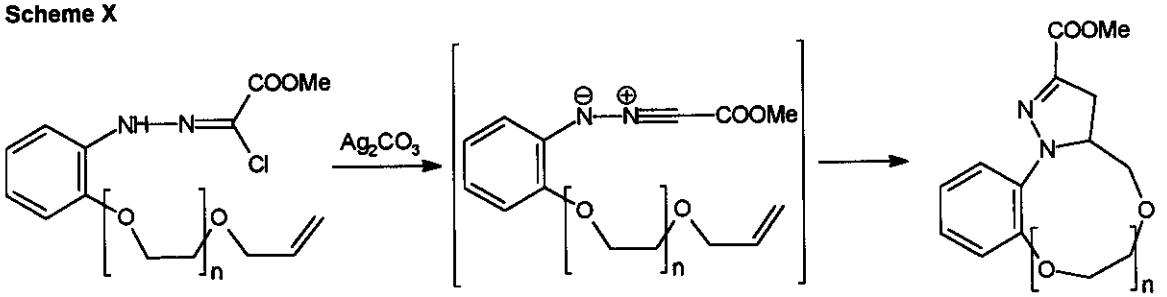
(ref. 57)



n	3	4
Yield (%)	47	43

(ref. 58)

Scheme X

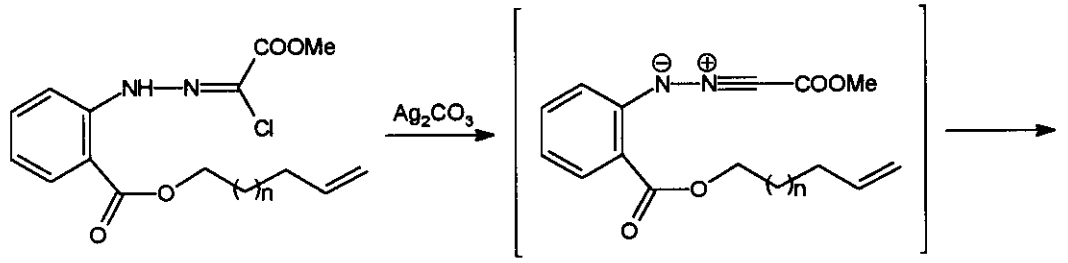


n	1	2
Yield (%)	46	39

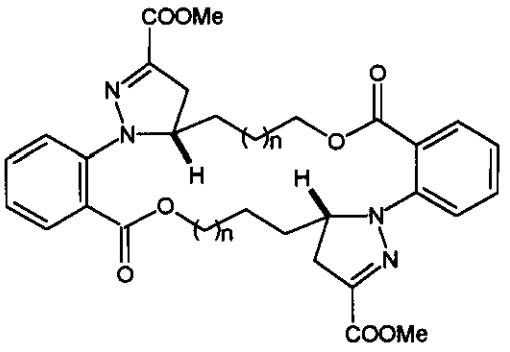
IV.5. Formation of Pyrazoles Annulated to a Large-sized Ring

A few independent research groups, on studying the behavior of functionalized 1,3-dipoles, have brought to light the possibility of an intermolecular plus intramolecular cycloaddition sequence leading to macrocyclic bis-heterophanes.[53,57,59-64] Of course, this sequence is competitive with the direct intramolecular cycloaddition and the predominance of one pathway over the other is markedly dependent on the length and the rotational freedom of the chain joining the reactive groups. An interesting case involving nitrilimines is outlined in Scheme XI.

Scheme XI



n	Yield (%)
3	5
6	4
7	4

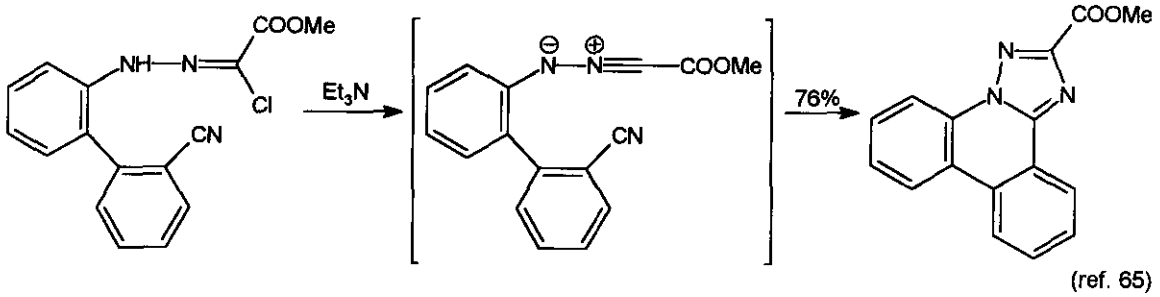


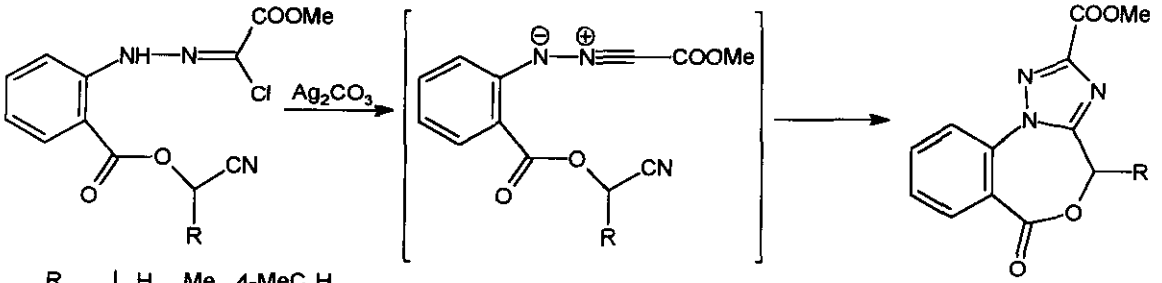
(ref. 57)

V. 1,3-DIPOLAR CYCLOADDITIONS TO CARBON-NITROGEN MULTIPLE BONDS

Intramolecular nitrilimine cycloadditions to the cyano group have been reported.[65-67] A number of them are illustrated in Scheme XII. It is worthy of noting that the usual regiochemistry leading to 1,2,4-triazoles does not find exception even at intramolecular level.

Scheme XII



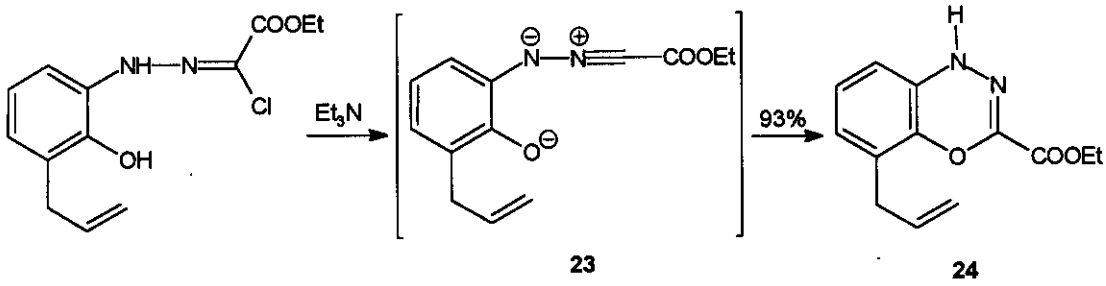


R	H	Me	4-MeC$_6$H$_4$
Yield (%)	32	18	28

VI. NUCLEOPHILIC ADDITIONS

This paragraph is concerned with nitrilimine cyclizations which are the consequence of an intramolecular nucleophilic attack to the carbon of the dipole. A typical case is the formation of 1*H*-4,1,2-benzoxadiazines (**24**) from nitrilimines (**23**), due to the nucleophilic participation of the phenoxide anion (Scheme XIII).[68]

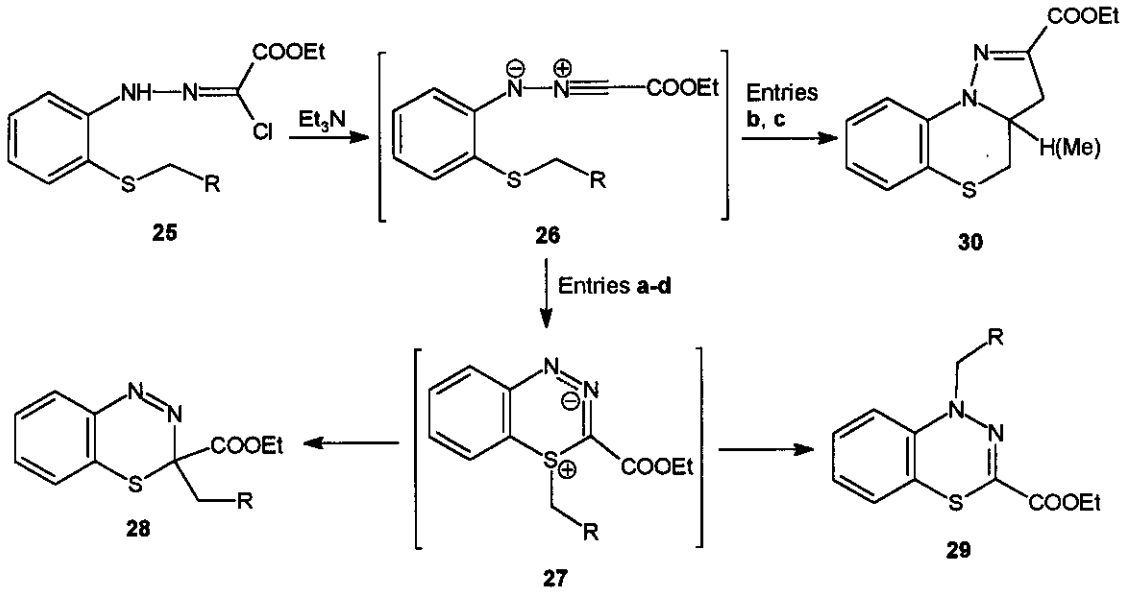
Scheme XIII



23 **24**

Nitrilimines (**26**), bearing a thioether function, exhibit a peculiar pattern of behavior (Scheme XIV).[69,70] The nucleophilic attack of the sulfur to the carbon of the dipole originates the cyclic sulfonium ylides (**27**), which then evolve *via* 1,2- and/or 1,4- shift of the *S*-pendant.

Scheme XIV



25 **26** **30**

28 **27** **29**

		Yield (%)		
Entry	R	**28**	**29**	**30**
a	Ph	33	36	--
b	$CH=CH_2$	70	--	7
c	$C(Me)=CH_2$	63	--	6
d	CN	--	15	--

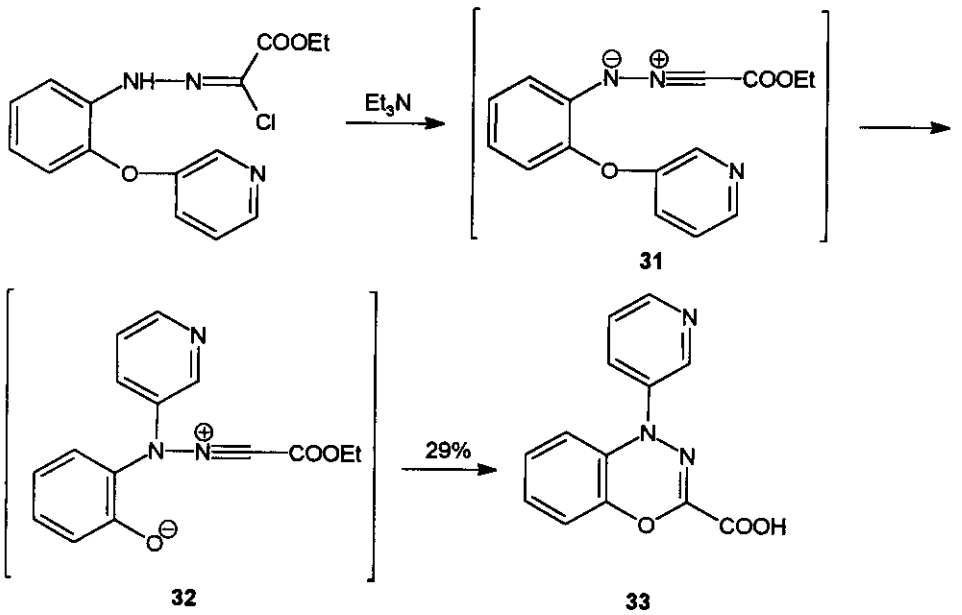
The hypotesis of the direct formation of **27** from **25** without the intermediacy of **26** must be discarded because the hydrazonyl chlorides (**25**) are inert in the absence of triethylamine. Surprisingly, the pathway going from **26** to **28** has appeared reversible. In fact, in the case of nitrilimines bearing both thioether and ethylene moieties, 3*H*-4,1,2-benzothiadiazines (**28**) are obtained under kinetic control, while the intramolecular cycloadducts (**30**) represent the thermodynamically favoured products.

Finally, the long-known rearrangement of *C*-(2-nitrophenyl) substituted nitrilimines finds explanation on assuming the initial nucleophilic participation of the nitro group.[71-73]

VII. ELECTROPHILIC ADDITIONS

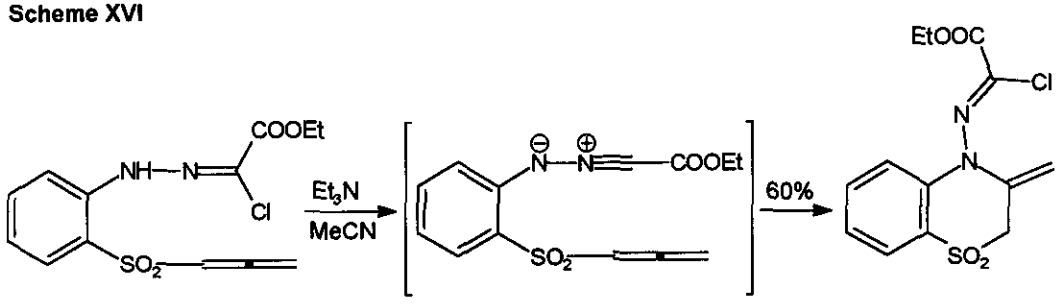
Although unusual, there are a few cyclization reactions characterized by intramolecular bond-forming between an electrophilic carbon and the azaanion-like nitrogen of the nitrilimine dipole. One case is given by the intriguing Smiles-type rearrangement of the nitrilimine (**31**) (Scheme XV).[74] Of course, the rearranged product (**32**) immediately closes to the *N*-substituted 1*H*-4,1,2-benzoxadiazine (**33**).

Scheme XV



A second case involves the central carbon of the strongly electron-poor allenic fragment of compound (**34**) (Scheme XVI).[75]

Scheme XVI



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ACKNOWLEDGEMENTS

Thanks are due to MURST (Rome) for financial support.

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Received, 10th February, 1997