

RECENT DEVELOPMENTS IN THE CHEMISTRY OF YLIDENE AZOLONES

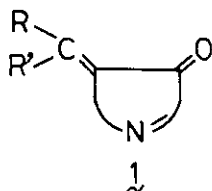
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Abstract - The recent developments in the chemistry of ylidene azolones are reported and the literature data were critically discussed.

INTRODUCTION:

α,β -Unsaturated azolones are versatile reagents and their chemistry has, in the past, received considerable attention. Interest in the chemistry of this class of compounds has recently been revived¹⁻⁸. Ylidene azolones have recently revealed several diverse interesting activities that have proved useful in heterocyclic synthesis⁹. Derivatives of the type **1** are generally obtained via condensation of active methylene heterocycles with aldehydes, ketones, orthoesters, amidines or nitriles. Such approaches are well familiar and known derivatives of several heterocyclic ring systems as well as their methods of preparation have been previ-



ously surveyed¹⁰. In the present manuscript we are going to survey relevant important developments and utilities of this class of compounds. It was not the plan to make an encyclopedic scan for the subject but rather to survey in one article the literature on this class of compounds. This survey seems to be useful for heterocyclic chemistry instructors, researchers and students.

CHEMICAL PROPERTIES AND REACTIONS:

In compounds **1** the presence of a keto group adjacent to an α,β -unsaturated linkage activates the latter toward nucleophilic reagents. Thus, such double bonded systems behave like chalcones, enamino ketones and the β -keto enols¹¹⁻¹⁴. Also

the presence of the α,β -unsaturated linkage activates the hetero ring toward a variety of reagents. The reactions that are going to be surveyed are those which take place at the double bond, at the ring carbonyl or on both moieties.

1- Reactivity toward active methylene reagents:

The exocyclic double bond in arylidene azolones has been observed to be highly active acceptor in Michael addition reactions.^{1,4,15-19} Thus, malononitrile, ethyl cyanoacetate and benzoylacetonitrile have been reported to add to the exocyclic

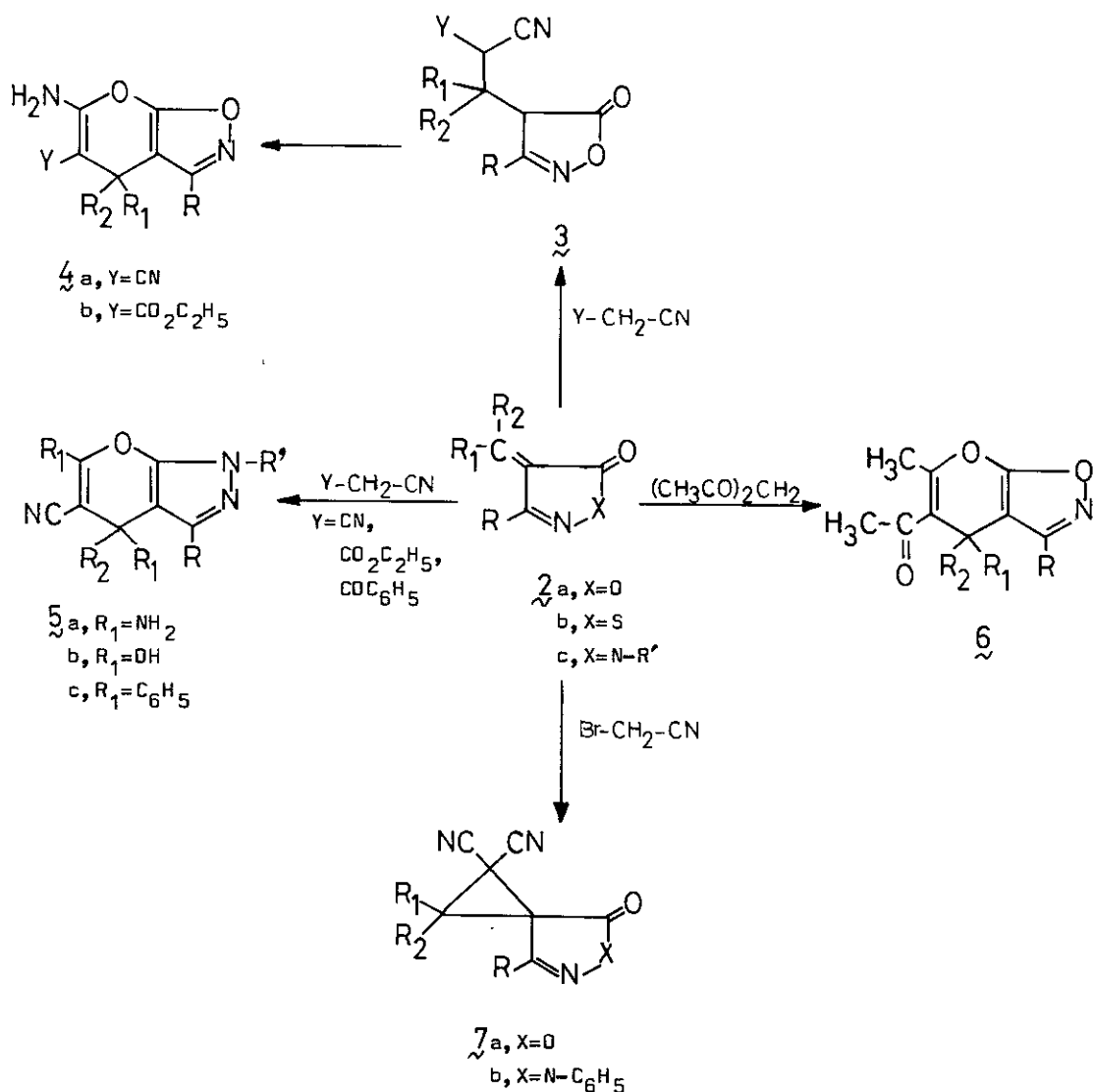


Chart 1

double bond in 4-arylidene-2-isoxazolin-5-one derivatives^{17,18} (2a) and in 4-arylidene-2-pyrazolin-5-one derivatives^{15,16} (2c). Harhash et al¹⁷ have assigned the acyclic structure 3 for the formed products. Recently, Otto-Schmeltz¹⁵ and Elnagdi et al^{4,19} have proved, based on ¹H-NMR data, that these adducts are in fact the isomeric cyclic enaminyopyrans 4 and 5. Acetylacetone afforded the pyrano [2,3-d]-isoxazole derivatives 6 on reaction with arylidene-isoxazolones under similar reaction conditions¹⁷.

The reaction of bromomalononitrile with 2a and 2c has been reported to afford the corresponding cyclopropane derivatives 7a,b²⁰ probably formed via intermediacy of the acyclic Michael type adducts similar to those postulated by Harhash et al¹⁷. However, the possibility that the dicyanocarbene is the reactive species can not be ruled out¹⁷ (cf. Chart 1). In contrast to these findings, Stachel et al²¹ have recently reported a novel pyrrole synthesis via reaction of 2-phenyl-4-arylidene-2-oxazolin-5-ones (8a) with ethyl cyanoacetate. The authors²¹ have shown that ethyl cyanoacetate effects ring cleavage of 8a to yield the isolable acyclic product 9 which could be cyclised into different pyrrolone derivatives (10 or 11) based on the cyclisation reaction conditions. The reactivity of 8a toward other activated methylene reagents has been recently investigated. Whereas the reaction with benzoylacetonitrile afforded the acyclic acid (12), the reaction with acetylacetone yielded the pyrano [3,2-d]oxazole derivatives 13²² (cf. Chart 2).

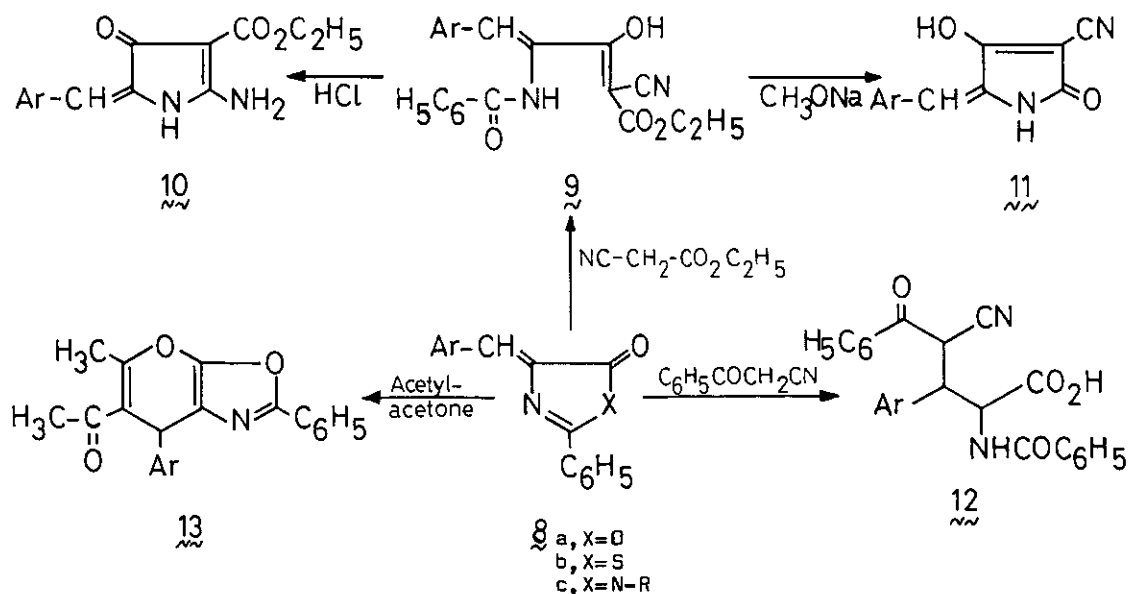
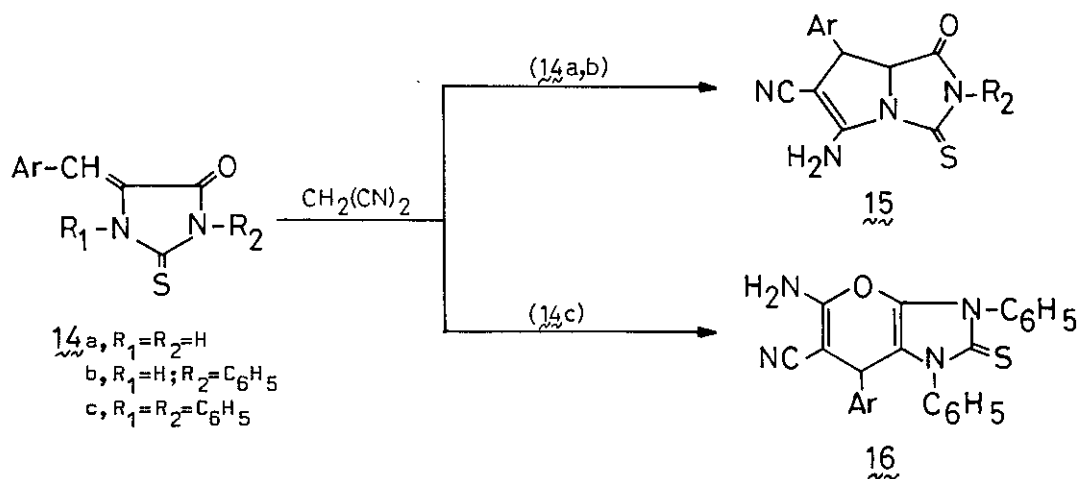
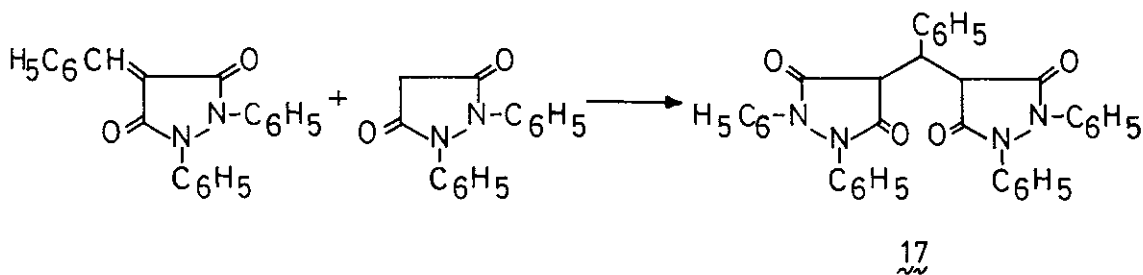


Chart 2

Recently, Daboun et al⁹ reported that 5-arylidene-4-imidazolidinone-2-thiones 14, reacted with malononitrile to give pyrrolo[1,2-c]imidazoles (15) or pyrano[2,3-d]-imidazoles (16) according to the absence or presence of substituents at position 1.



The double bond in arylidene azolones has been also reported to add to the active methylene azolones²³⁻²⁵ to afford bis-adducts as shown from the following example:



Similar to the behaviour of benzylidene azolones, 1-phenyl-3-methyl-5-dimethylaminomethylene-2-pyrazolin-5-one reacted with active methylene reagents to give the pyrano[2,3-c]pyrazoline derivatives (18) probably formed via Michael type addition, elimination of dimethylamine and cyclisation (cf. Chart 3).²

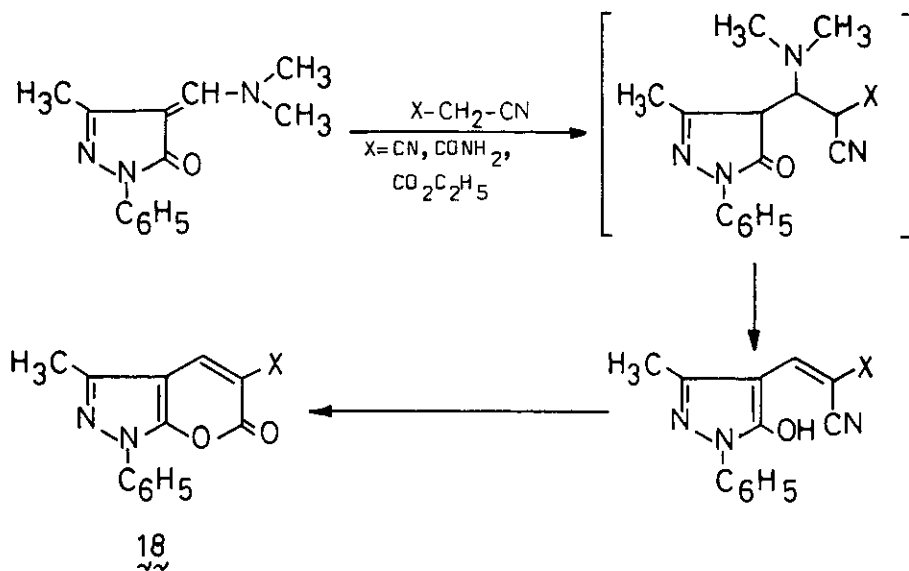
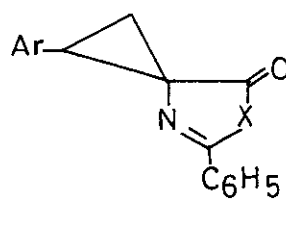
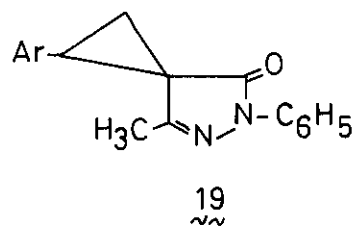


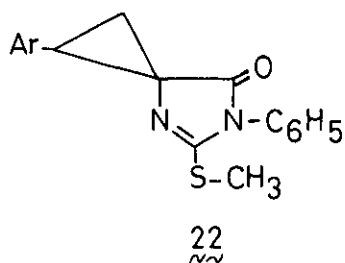
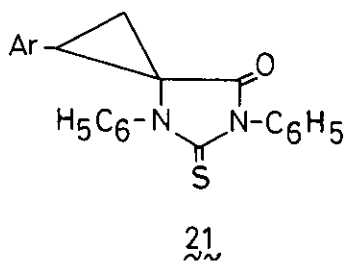
Chart 3

2- Reactions with diazomethane:

1-Phenyl-3-methyl-4-arylidene-5-pyrazolones (2c), 4-arylidene-2-oxazolin-5-ones (8a), 4-arylidene-2-thiazolin-5-ones (8b), 1,2-diphenyl-4-arylidene-2-imidazolin-5-ones (8c) and 1,3-diphenyl-5-arylidene-4-imidazolidinone-2-thione (14c) reacted with diazomethane to afford the corresponding cyclopropane derivatives 19, 20a,b,d and 21 respectively²⁶⁻³⁷. On the other hand, methylation as well as cyclopropane formation were observed when 2-phenyl-4-arylidene-2-imidazolin-5-ones (8c, R=H)³⁴ and 3-phenyl-5-arylidene-4-imidazolidinone-2-thione (14b)³⁶ reacted with ethereal



20a, X=O
 b, X=S
 c, X=N-CH₃
 d, X=N-C₆H₅

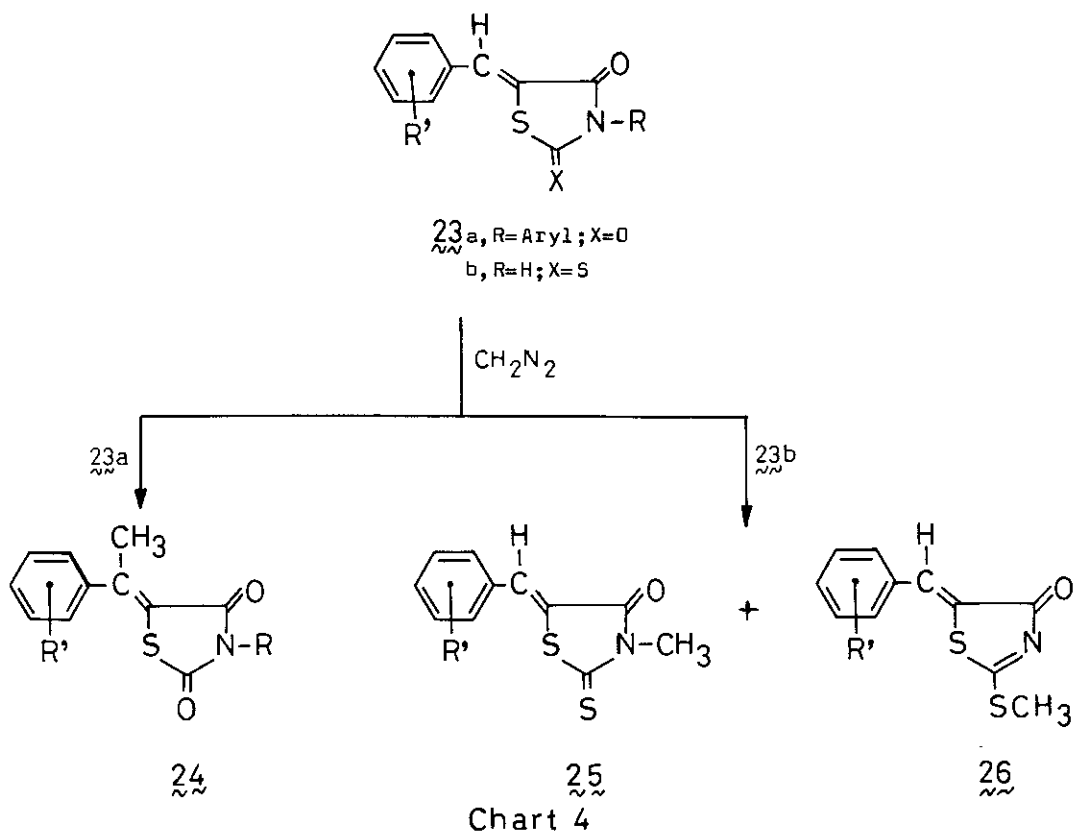


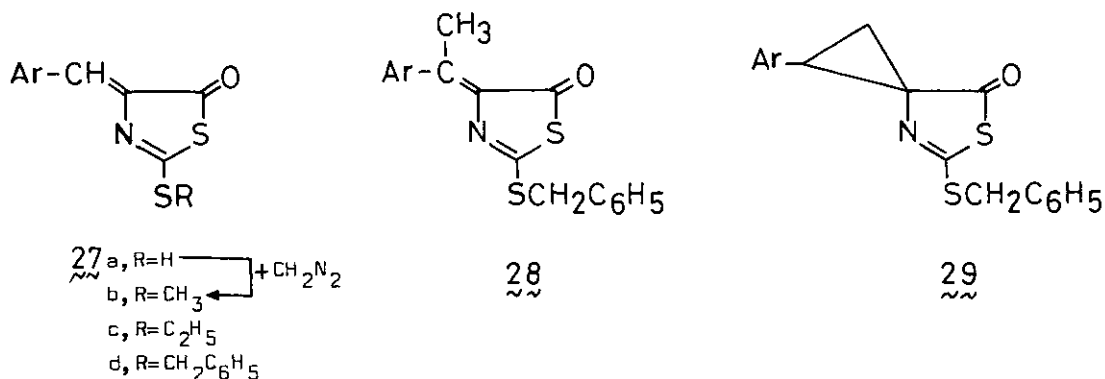
diazomethane to afford $\underline{20c}$ and $\underline{22}$ respectively.

In contrast to the above mentioned observations, 3-aryl-5-arylidene-2,4-thiazolidenediones ($\underline{23a}$) reacted with ethereal diazomethane to yield the corresponding C-methylated derivatives ($\underline{24}$)³⁸.

Treatment of 5-arylidene-4-thiazolidinone-2-thione ($\underline{23b}$) with gaseous diazomethane gave mixtures of N-methyl and S-methyl derivatives ($\underline{25}$ and $\underline{26}$)³⁹. A linear correlation exists between the log of the relative yields (N-methyl/S-methyl) and substituent constants of the substitution group R'. Increasing the dielectric constants of the solvents increased the relative yields of N-methyl derivatives. In amines like triethylamine and aniline, only the S-methylthiazolone derivative is the sole isolable reaction product (cf. Chart 4).

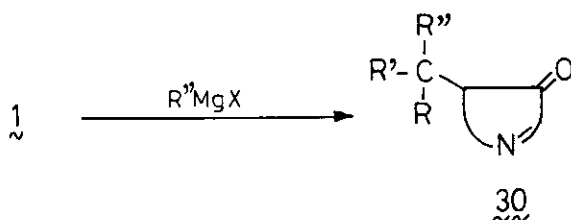
It has been reported also that the exocyclic double bond in $\underline{27a}$ appears stable toward the action of ethereal diazomethane and only the S-methyl derivatives $\underline{27b}$ were formed⁴⁰. On the other hand, 2-benzylmercapto-5-arylidene-2-thiazolin-5-ones ($\underline{27d}$) afforded the C-methyl derivatives $\underline{28}$ together with the cyclopropane derivatives $\underline{29}$ on treatment with the same reagent⁴¹.



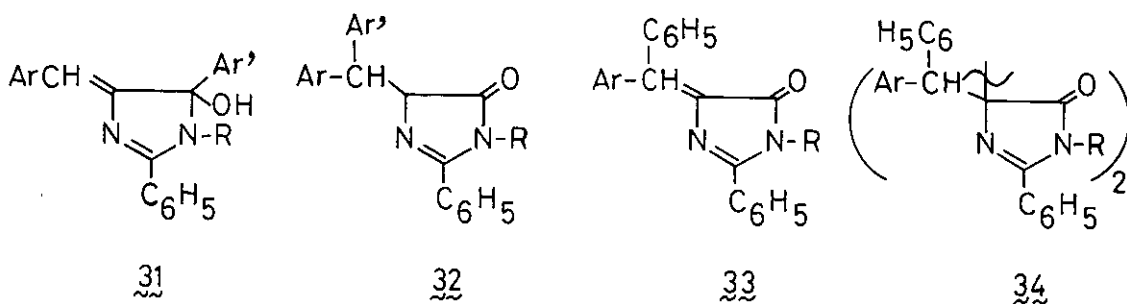


3- Reactions with Grignard reagents:

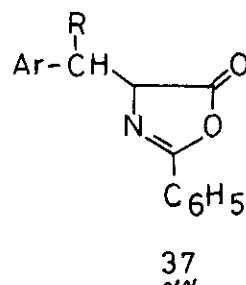
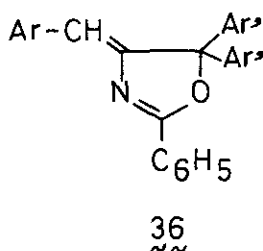
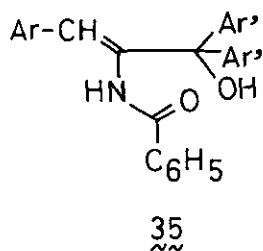
α,β -Unsaturated azolones are well known to undergo 1,4-addition of Grignard reagents on the activated double bond leading to the formation of saturated 4-aryl or alkyl substituted azolones (30).^{24, 25, 36, 37, 42-70} Mustafa and Harhash⁷¹ have reported that 4-arylidene-2-imidazolin-5-ones ($8c$) reacted with Grignard reagents via 1,2-addition of the reagent to the carbonyl group to afford the corresponding hydroxyimidazole derivatives 31 . However, Awad et al⁴² have corrected



the structure of these products and proved that the reaction is really a typical 1,4-addition affording 32 . These results were confirmed later when Asker et al^{66, 72} found that phenylmagnesium bromide reacted with $8c$ on the cold to give 32 (Ar'=Ph). On the other hand, compound 32 together with its oxidation products 33 and 34 were obtained when the reaction was conducted at the boiling point of the solvent.



Whereas the oxazolone ring in 2-phenyl-4-arylidene-2-oxazolin-5-ones (8a) is readily opened by the action of arylmagnesium halides to give 1,1-diaryl-2-benzoylaminocinnamyl alcohol derivatives (35) together with 2-phenyl-4-arylidene-5,5-diaryl-2-oxazolines (36),^{71,73,74} 1,4-addition of the reagent to the double bond conjugated with the carbonyl function, takes place upon treatment of 8a with

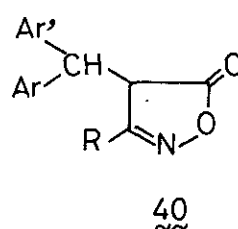
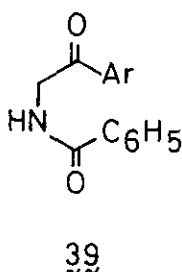
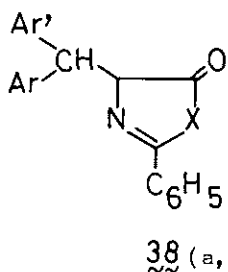


alkyl- and aralkylmagnesium halides to give 37^{62,63}. No tertiary alcohol (or the corresponding thiazoline), which would have been formed by the 1,2-addition could be detected.

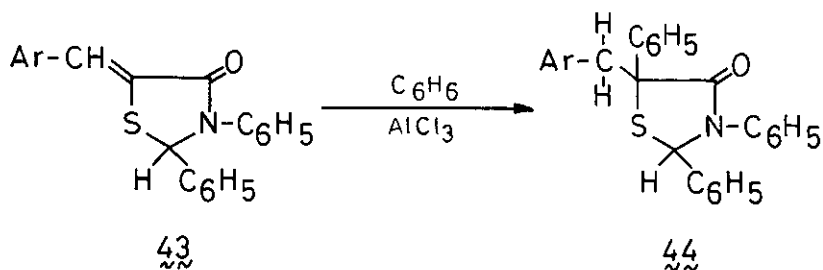
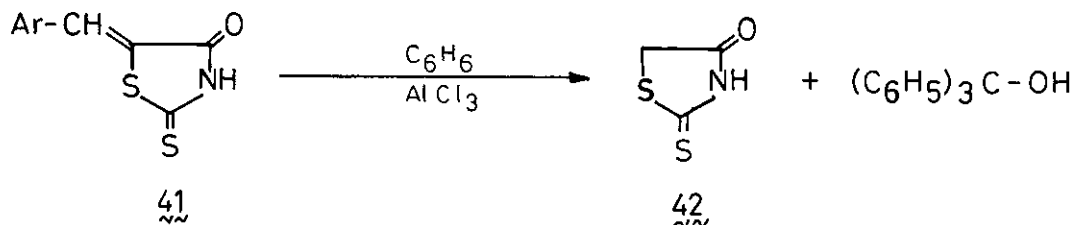
4-Friedel-Crafts reactions:

Treatment of 2-phenyl-5-arylidene-5(4H)-oxazolones (8a) with aromatic hydrocarbons in the presence of anhydrous aluminium chloride results in the formation of either 38a, formed by 1,4-addition of the hydrocarbon to the α,β -unsaturated system, or 39, formed via arylation and arylidene cleavage, depending upon several factors. Among these factors are the ageing of aluminium chloride, the temperature of the reaction and the presence of traces of moisture.^{62,75,76}

When 4-arylidene-2-isoxazolin-5-ones (2a)^{56,57} and 2-phenyl-4-arylidene-5(4H)-thiazolone (8b)⁶¹ were treated with benzene in the presence of anhydrous aluminium chloride, 1,4-addition to the α,β -unsaturated carbonyl system took place with the formation of 40 and 38b. No products resulting from arylation or arylation and benzylidene cleavage have been isolated⁶¹.



Snider et al⁷⁷ reported that the reaction of 5-arylidene-4-thiazolidinone-2-thione (41) with benzene and ≥ 4 mol of aluminium chloride cleaved the arylidene substit-



uent to give 4-thiazolidinone-2-thione (42) and triphenylcarbinol.

Under similar conditions, 2,3-diphenyl-5-arylidene-4-thiazolidinones (43) added benzene to the unsaturated linkage to give the 2,3,5-triphenyl-5-arylmethyl-4-thiazolidinone derivatives 44.⁷⁷

5- Reactivity in dipolar cycloaddition reactions:

Ylidene azolones seem to be interesting dienes and dienophiles. In this respect they can be considered as excellent starting materials in dipolar cycloaddition reactions. The utility of these reagents in the latter reactions has received relatively little attention. An interesting reaction of 3-phenyl-4-benzylidene-2-isoxazolin-5-one with α -chlorobenzaldehyde phenylhydrazone leading to the formation of 1,3,4-triphenylpyrazole-5-carboxylic acid (46) has been reported⁷⁸. The reaction is believed to proceed via the intermediacy of the spiro compound 45 which could not be isolated⁷⁸.

However, the reaction of the same benzylidene with benzonitrile oxide afforded the isolable spiro isoxazole derivative 47⁷⁹ (cf. Chart 5).

Other spiro pyrazoloneisoxazolines (48 and 49) have been also isolated from the reaction of 4-benzylidene-5-pyrazolones with N-oxides⁸⁰⁻⁸².

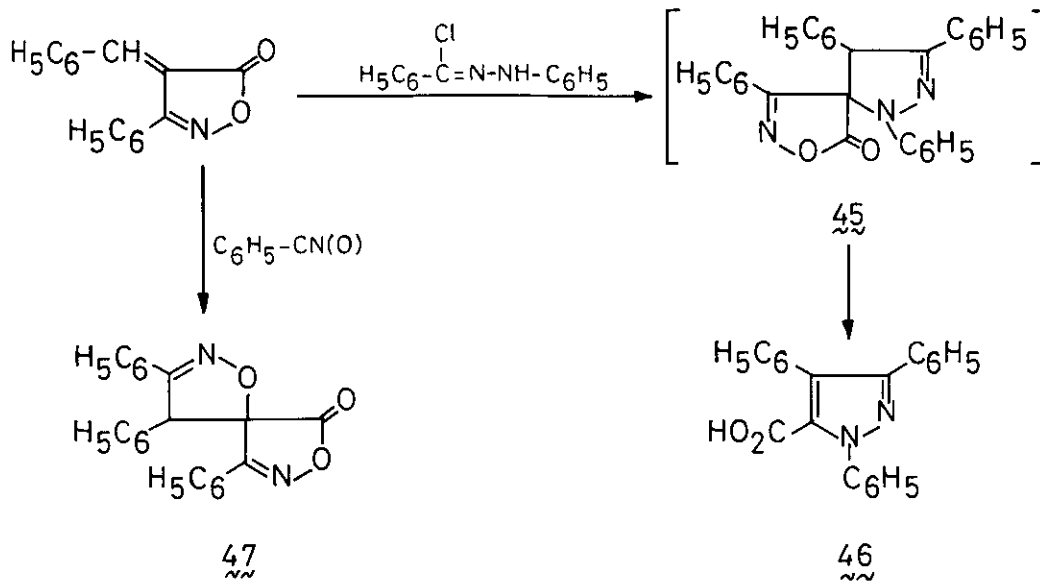
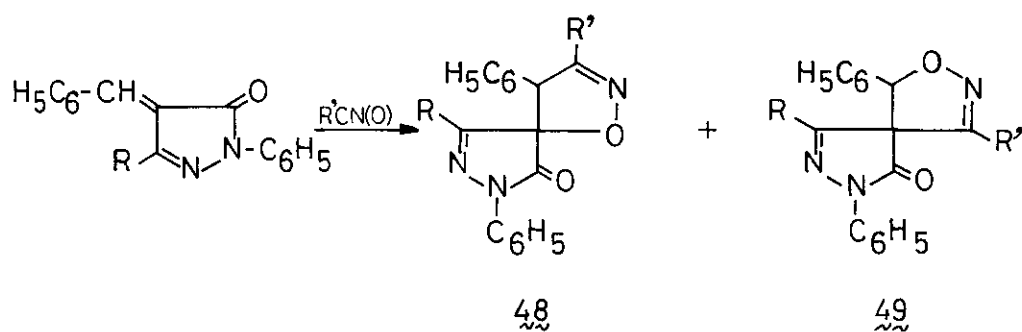
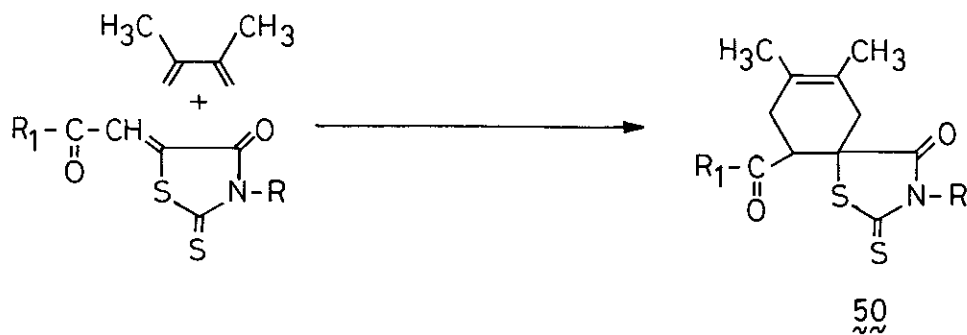


Chart 5

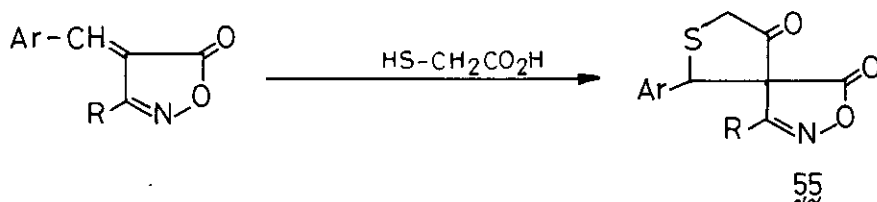


The exocyclic double bond in 5-(aroylmethylidene)-4-thiazolidinone-2-thiones added 2,3-dimethylbuta-1,3-diene to give the thiazolidinone spirocyclohexene derivatives 50.⁸³



same reaction conditions⁸⁶. Similar behaviour has been also reported with 2-ethylmercapto-4-isopropylidene-2-thiazolin-5-one⁸⁷.

Thioglycollic acid reacted with 4-arylidene-2-isoxazolin-5-ones to afford the



spiro products 55¹⁷. The reaction probably proceeds via addition of the reagent to the exocyclic double bond followed by water elimination.

7- Reduction:

Reduction of 4-benzylidene-2-imidazolin-5-one afforded different products depending upon the applied reaction conditions. Thus, reduction using zinc dust and acetic acid resulted in saturation of the ring double bond with the formation of 56⁸⁸. When using palladium oxide in the presence of hydrogen and ethanol, saturation of the exocyclic double bond takes place to afford 57⁸⁹. On the other hand, saturation of both ring and exocyclic double bonds took place on using sodium amalgam in ethanol to yield 2-phenyl-4-benzyl-5-imidazolidone (58)⁸⁹. Compound 58 could also be obtained by reducing 1-hydroxy-4-benzylidene-2-imidazolin-5-one with sodium amalgam in ethanol⁹⁰ (cf. Chart 6).

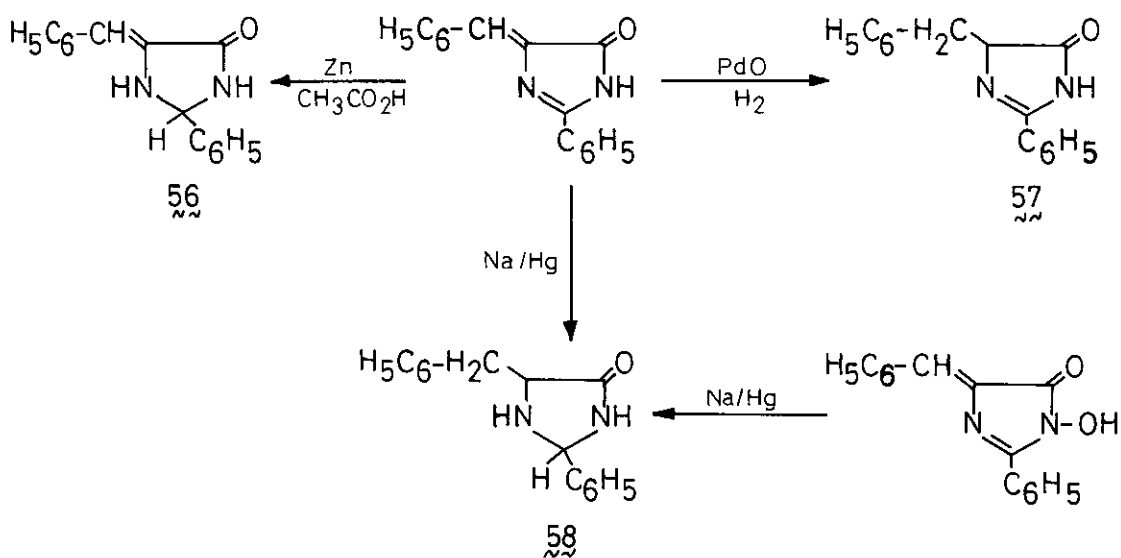
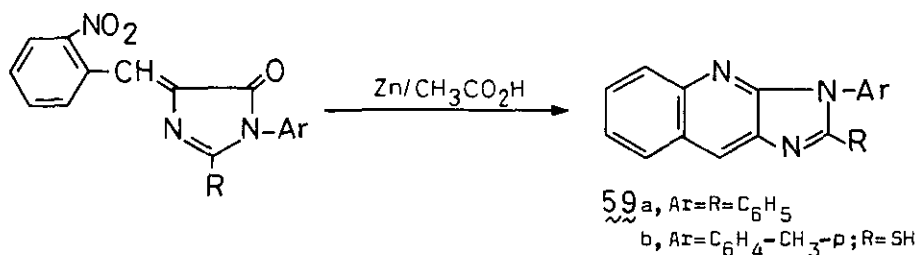


Chart 6

Treatment of the 4-nitrobenzylidene-5-imidazolone derivatives with zinc dust and acetic acid afforded the imidazolinoquinoline derivatives 59^{91,92}.



Kametani et al⁹³ found that treatment of 2-phenyl- and 2-methyl-4-(4,5-dialkoxy-2-nitrobenzylidene)oxazol-5-ones (60) with triethyl phosphite afforded the corresponding 2-phenyl- and 6,7-dialkoxy-2-methyloxazo[5,4-b]quinolines (62), respectively. The simplest mechanism accounting for the formation of 62 involves initial reduction of the nitro group and formation of the nitrene 61, followed by one or

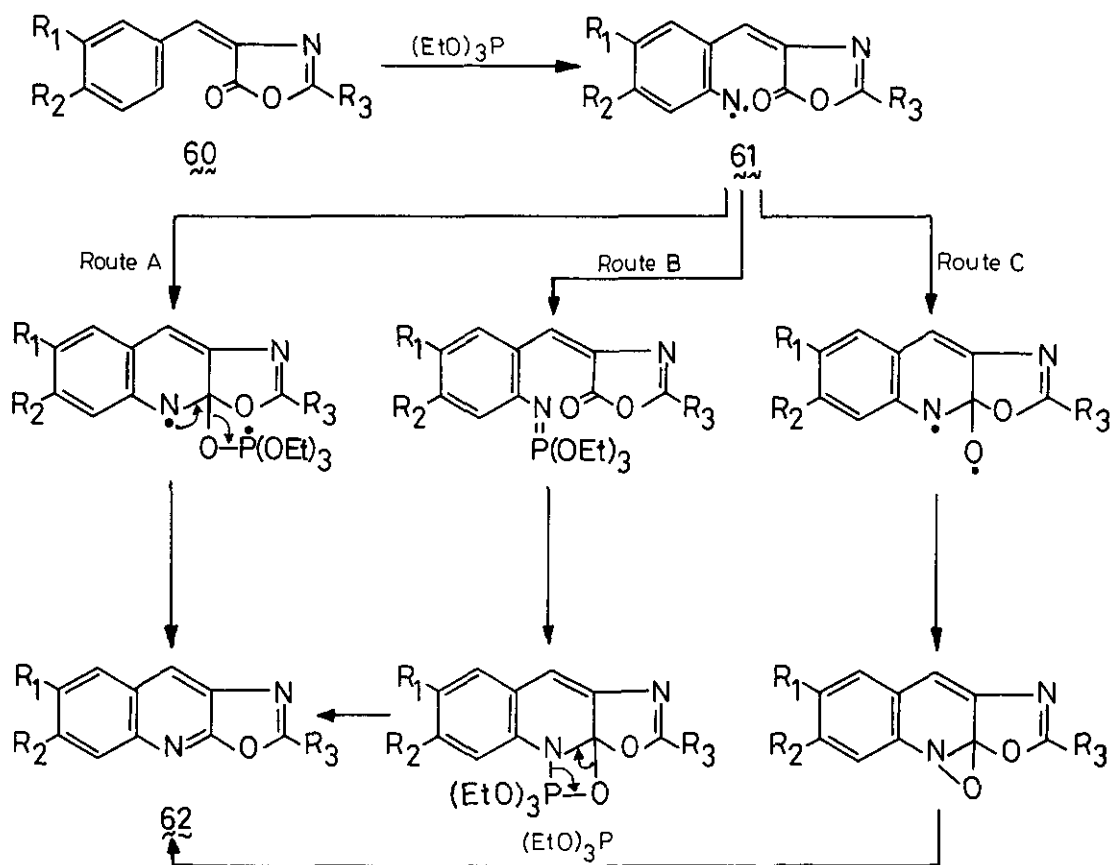


Chart 7

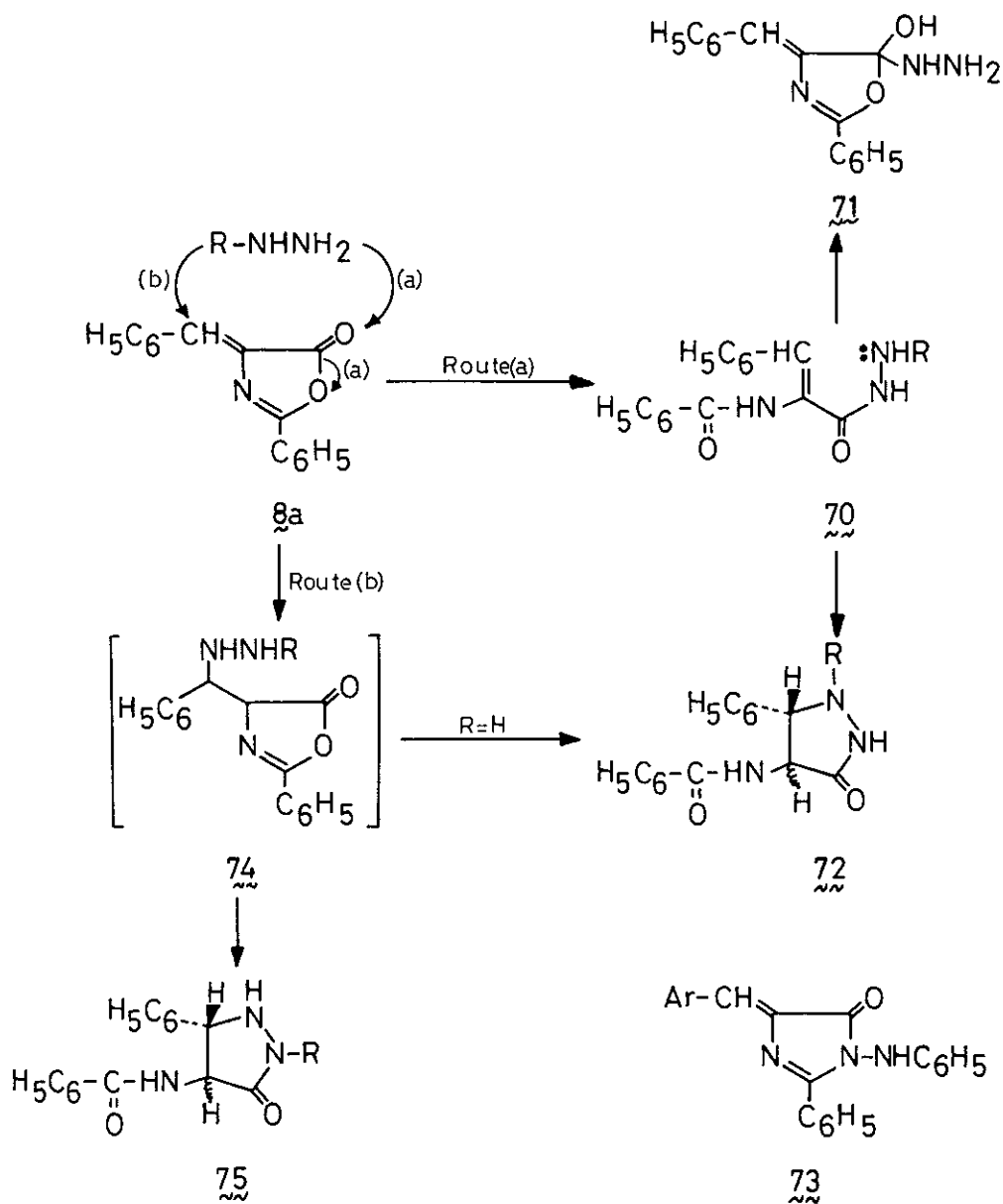
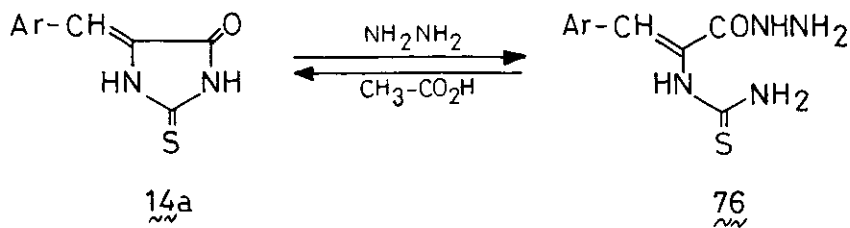


Chart 10

intermediacy of the isolable Michael adducts 70 (route a) whereas compounds 75 were formed, more probably, via the formation of the intermediates 74 (route b) (cf. Chart 10).

5-Arylidene-4-imidazolidone-2-thiones were converted into the hydrazides 75 on treatment with hydrazine hydrate. The latter 75 could be converted back into the starting materials when treated with acetic acid¹⁰¹.



Recently, Daboun and Ibrahim¹⁰² reported an interesting rearrangement reaction of 1-aryl-2-methylmercapto-4-arylidene-2-imidazolin-5-ones (77) into 1-amino-2-aryl-imino-4-arylidene-5-imidazolidinones (78). The reaction was suggested to proceed

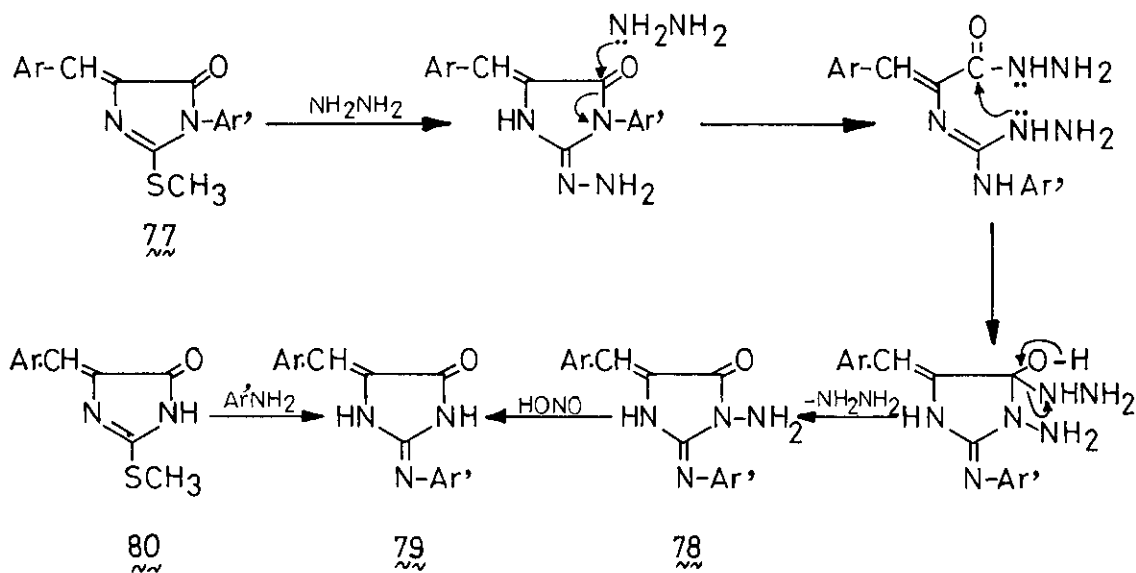
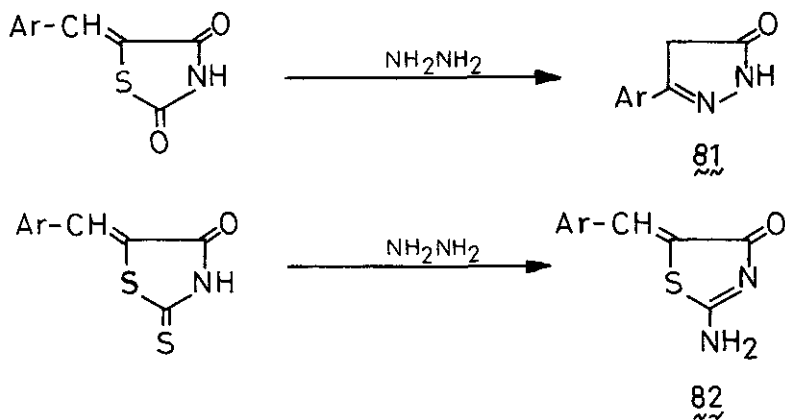


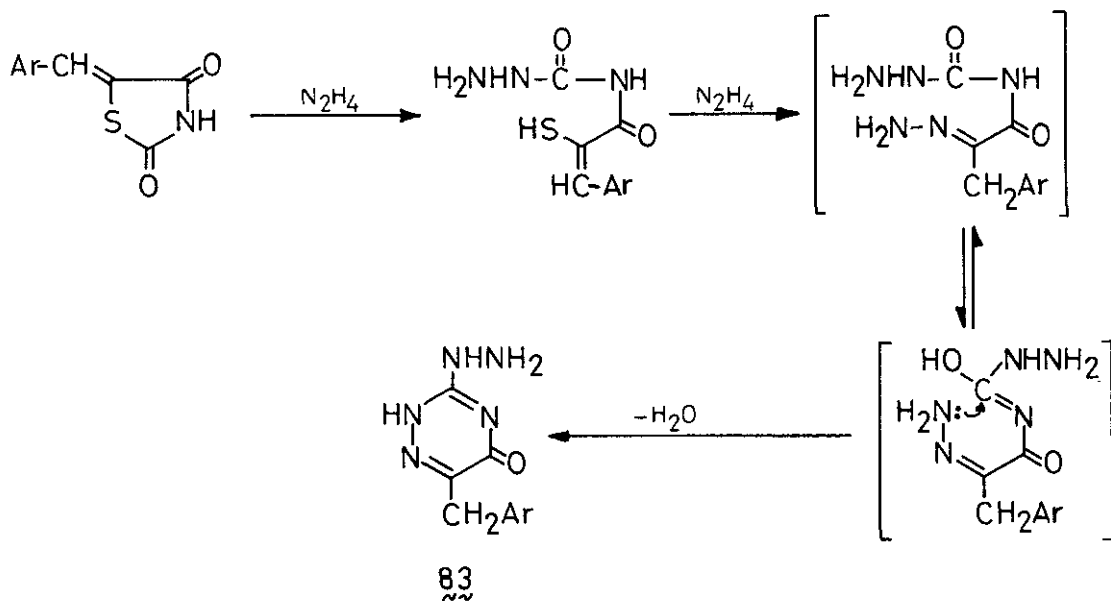
Chart 11

via the mechanism demonstrated in Chart 11. The formed products 78 were deaminated to 79 by the action of nitrous acid. Compounds 79 were also obtained via independent synthesis by the action of aromatic amines on the 2-methylmercapto-4-arylidene-2-imidazolin-5-one derivatives 80.

5-Arylidene-2,4-thiazolidinediones react with hydrazine to undergo ring cleavage followed by cyclisation to yield 5-aryl-3-pyrazolinones (81) in 55-70% yields. On the other hand, 5-arylidene-4-thiazolidinone-2-thiones on treatment with hydrazine gave 2-amino-4-arylidene-4-thiazolinones (82) in 35-50% yields¹⁰³.



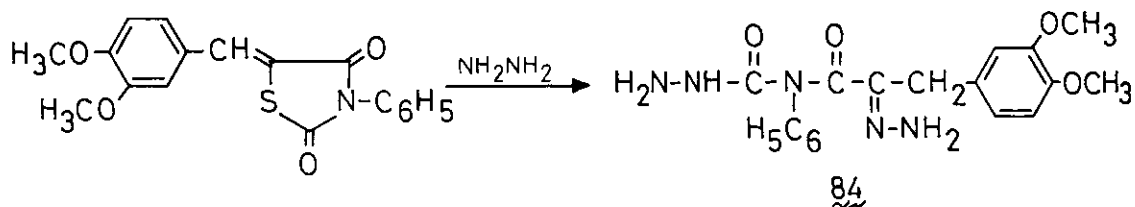
However, Raouf et al¹⁰⁴ reported the synthesis of the triazinones 83 by the reaction of 5-(substituted benzylidene)-2,4-thiazolidinediones with hydrazine. The route



(Ar=6-Bromo-3,4-methylenedioxyphenyl,
6-Bromo-3,4-dimethoxyphenyl)

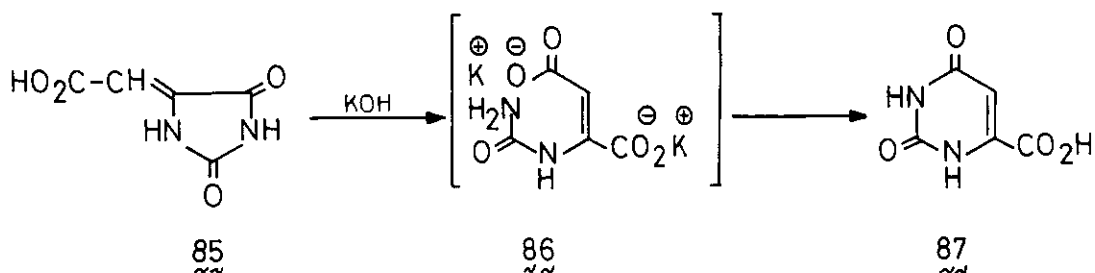
Chart 12

through which the transformation occurs is demonstrated in Chart 12. Ring cleavage of 5-(3,4-dimethoxybenzylidene)-3-phenyl-2,4-thiazolidinedione can be affected by the action of hydrazine to give 1-amino-3-phenyl-5-[[[(3,4-dimethoxyphenyl)ethylidene]amino]biuret] (84) with the evolution of hydrogen sulphide.¹⁰⁴



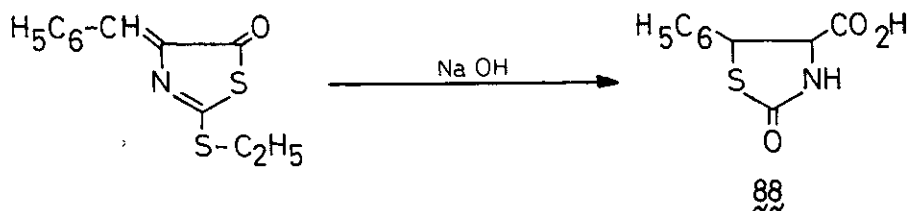
9- Miscellaneous:

Several unusual reactions have been reported for ylidene azolones. The most interesting of these reactions will only be discussed here. It has been found that 5-carboxymethylidene-2,4-imidazolidinedione (85) reacted with boiling potassium hydroxide

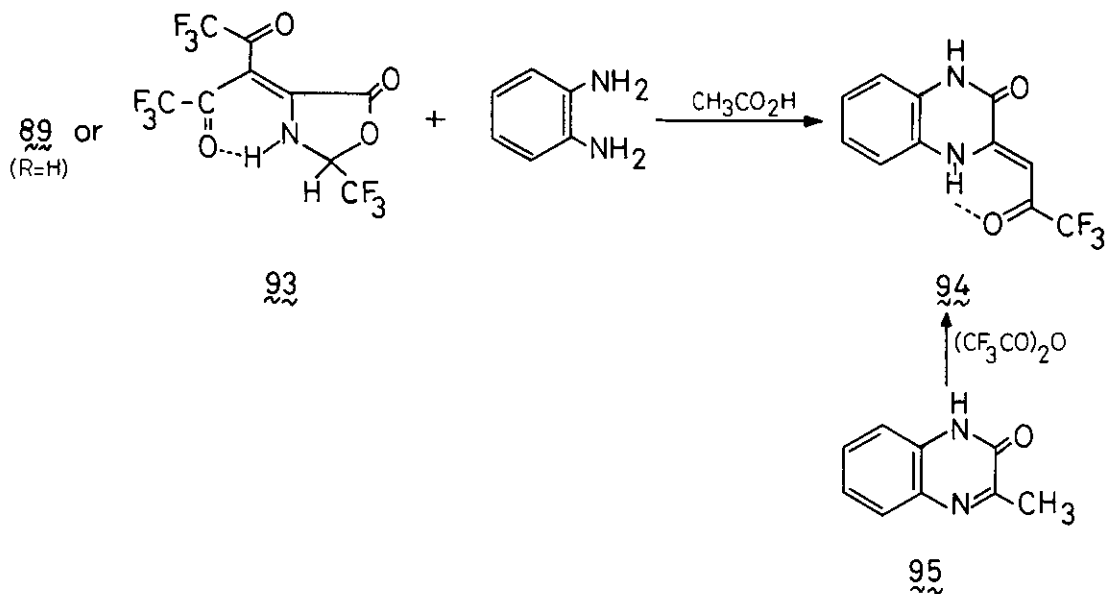


solution with ring expansion to yield the pyrimidine derivative, orotic acid, 87. The reaction probably proceeds via the formation of the non-isolable intermediate salt 86^{105,106}.

Treatment of 2-ethylmercapto-4-benzylidene-5(4H)-thiazolone with sodium hydroxide solution afforded 4-carboxy-5-phenyl-2-thiazolidone (88). This rearrangement reaction proceeds via a hetero-ring opening, elimination of ethylmercaptan and subsequent recyclicalisation^{86,87}.



2-Trifluoromethyl-4-trifluoroacetylmethylene-5-oxazolidones (89) are converted into the 2-trifluoromethyl-4-trifluoroacetamino-2,5-dihydro-5-furanone derivatives (92) when they are heated for a long period at about 100°C. The rate of the reaction is strongly enhanced by the addition of an amine. These results make the mech-



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