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The Chemistry of [1,2,3]Triazolo[1,5-*a*]pyridines

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The reactivity of [1,2,3]triazolo[1,5-*a*]pyridines 1 is described. Triazolopyridines react with electrophiles in two contrasting ways, giving 3-substituted triazolopyridines 2, or products 3, resulting from triazolo ring opening with loss of molecular nitrogen. The triazolopyridines can be lithiated at −40°C by lithium diisopropylamide in ether giving regiospecifically the 7-lithio derivative. Bromotriazolopyridines have activation towards nucleophilic substitution at position 5 and 7, and benzenoid inertness at position 6. The parent compound 1a is easily hydrogenated giving tetrahydrotriazolopyridine 11a in high yield; when the triazolopyridines have substituents, the hydrogenation reaction strongly depends on the position of the substituent. Triazolopyridinium ylides of type 18 and 26 react with acetylenic esters; these reactions are influenced by the nature of solvent and the acetylenic ester used, giving different types of adducts: stable disubstituted triazolopyridinium ylides of type 19 and 20, indolizines 21, or pyrroleninylpyrazolo[5,1-*a*] pyridines 22. Photochemistry, and photochemical reactions with MP and DMAD of these ylides are also described. A new way to 2,2′-bipyridines, in two steps from triazolopyridines is reported.

Keywords: Triazolopyridines; Triazolopyridinium ylides; Lithiation reactions; Bipyridines

INTRODUCTION

The general class of triazolopyridines includes five heterocyclic systems. Three of these systems are 1,2,3-triazoles and two are 1,2,4-triazoles. Three have bridgehead nitrogen, and two do not. In general this last division reflect differences in synthesis or in properties. The discovery of trazodone, a [1,2,4]-triazolopyridine, as a selective serotonin reuptake inhibitor,[1] and its approval for the treatment of depression, has stimulated interest in triazolopyridines in general. In particular, we are interested in the chemistry and potential applications of [1,2,3]triazolo[1,5-*a*]pyridine **1a** and its derivatives. Our work is a contribution to the study of the unknown reactions of [1,2,3]triazolo[1,5-*a*]pyridines, small but versatile compounds that have led us to discover an interesting field of research. This is a short review of their chemistry.

REACTIONS WITH ELECTROPHILES

The [1,2,3]triazolo[1,5-*a*]pyridines can be synthesized by the Bower procedure[2] to get triazolopyridines from an oxidation of the hydrazone of a pyridine-2-aldehyde or ketone. The study of their chemistry was started by Jones *et al.*[3] with the reactions with electrophiles. Triazolopyridines react with electrophiles, other than alkylating agents, in two contrasting ways: Vilsmeier formylation and nitration give 3-substituted triazolopyridines **2**;[3] other electrophiles like halogens, mercuric acetate, aqueous sulphuric acid, glacial acetic acid and selenium dioxide, give products **3**,[4] resulting from triazolo ring opening with loss of molecular nitrogen (Figure 1).

The following mechanism was proposed to explain these results.[3] The formation of pyridine derivatives with loss of nitrogen must be attributed to the tautomerism (**1** ⇄ **4**), or, more likely, to the tautomerism of the intermediate (**5** ⇄ **6**) in

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Abbreviations: (DBTCE), 1,2-Dibromo-1,1,2,2-tetrachloroethane; (DMAD), Dimethyl acetylene-dicarboxylate; (DMF), Dimethylformamide; (MP), Methyl propiolate; (NBS), *N*-bromosuccinimide; (NO), Nitric oxide; (TCNEO), Tetracyanoethyleneoxide; (THF), Tetrahydrofuran

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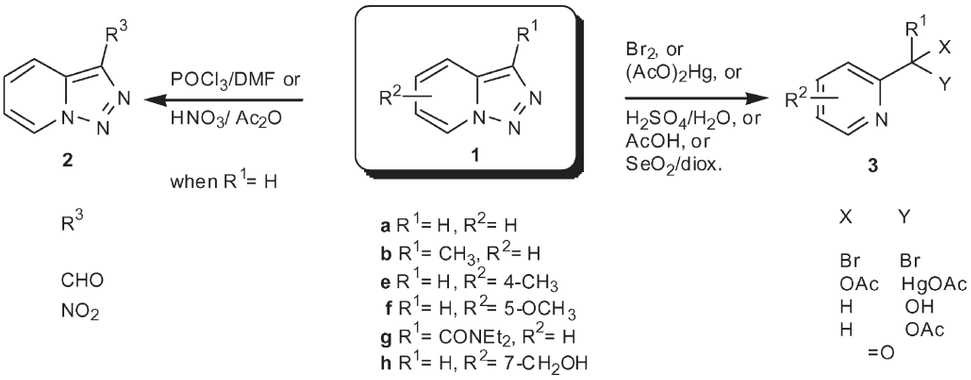


FIGURE 1

electrophilic substitution. If the electrophile E is an electron-withdrawing group, the intermediate will be more stable and deprotonation of the cyclic form competes successfully with loss of nitrogen. If the electrophile E is only weakly stabilising the diazonium intermediate, nucleophilic attack with loss of nitrogen is the favoured process. (Scheme 1).

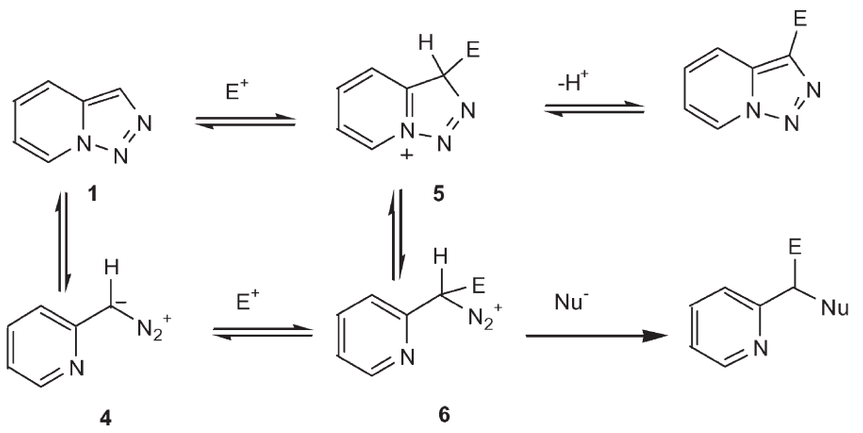
Of the three nitrogen atoms in triazolopyridines, two would appear to be available sites for protonation or for reaction with alkylating agents. We have been able to verify the site of protonation and alkylation as N2;[5] an observation supported by molecular orbital calculations.[6] We have prepared a large number of triazolopyridinium quaternary salts of the parent **1**, 3-alkyl, 3-arylderivatives and 7-aminotriazolopyridines, and shown that quaternization is possible on both sites if sufficient hindrance is present, as in the case of alkylation of 3-*t*-butyltriazolopyridine.[5] Prolonged treatment with methyl iodide in acetone gave a mixture of N1 and N2 quaternary salts in a 1:4 ratio.

Coordinating behaviour of 3-methyltriazolopyridine with transition metal ions has been investigated. The 3-methyl derivative coordinates to a copper(II) ion through a single nitrogen atom described as monodentate. The molecular structure has been determined by X-ray diffraction methods. As in the protonation and quaternization, the donor atom is N2.[7]

LITHIATION REACTIONS

The triazolopyridines can be lithiated at −40°C by lithium diisopropylamide in ether giving regiospecifically the 7-lithio derivative; this lithiation position must be directed by the "peri" nitrogen atom, because in the parent compound, deuterium exchange normally occurs first at position 3 under basic conditions. The 7-lithio derivatives reacted with various aldehydes and ketones to give triazolopyridin-7-ylmethanols[8,9] (Figure 2).

The structure of these compounds attracted the attention of a Pharmacology Group in our University, working in the field of cardiovascular drugs under the direction of Professor Pilar D'Ocón.



SCHEME 1

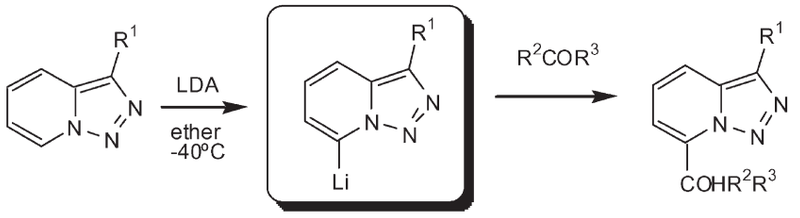


FIGURE 2

In preliminary tests, potential myorelaxing properties of these compounds were evaluated on isolated rat aorta and their ability to displace ^{3}H-prazosin, ^{3}H-diltiazen and ^{3}H-nitrendepine was determined. Neither myorelaxing activity, nor displacement of the tested radioligands was observed at concentrations from 10^{-8} to 10^{-4} M.[10]

SYNTHESIS OF 2,6-DISUBSTITUTED PYRIDINES

The combination of these two series of experiments, regioselective lithiation and treatment with electrophiles, followed by triazolo ring opening reaction, opened the way to a general synthesis of 2,6-disubstituted pyridines using the triazolopyridines as a synthon (Figure 3).[8–11]

REACTIONS WITH NUCLEOPHILES

We considered that the synthesis of 2,6-disubstituted pyridines would be considerably improved if nucleophilic substitution could also be achieved on the triazolopyridines. The synthesis would be completely general. We have achieved this generality *via* the introduction of a bromine substituent into position 7 on triazolopyridines, and displacement of the bromine atom by nucleophiles. After triazolo ring opening, a range of 6-substituted pyridine-2-aldehydes or ketones become available.

We had different approaches to produce such bromotriazolopyridines, ultimately successful. We first attempted to prepare 7-bromotriazolopyridine by treating the 7-lithio derivative with bromine at −40°C, but even at this low temperature rapid and substantial ring opening occurs, leading to 6-bromo-2-dibromomethylpyridine as the major product. We also investigated the reaction of the 3-methyl-7-lithio derivative with bromine. Although the major product recovered was the starting triazolopyridine and polymerisation occurred, a small amount (5%) of a monobromotriazolopyridine, the 7-bromoderivative, could be isolated; a second product, formed in approximately the same yield (6%), was the derivative resulting from triazolo ring opening. Carrying out this reaction with 7-lithio-3-(*N*,*N*-diethylcarbomoyl)triazolopyridine afforded three isomeric products: the 7-bromo derivative, obtained in a 10 % yield, the 6 and the 4-bromo derivatives.

In a parallel approach to the 7-bromotriazolopyridines, we have studied the preparation and properties of the trimethylsilyl derivatives. They were obtained in good yield from the appropriate lithio derivative and trimethylsilyl chloride. It is known that trimethylsilyl groups react with bromine to give aryl bromides, but we have discovered that trimethylsilyl substituents, adjacent to bridgehead nitrogen in triazolopyridines, are very stable. Treatment with bromine in carbon tetrachloride gave the open ring derivatives.[12]

Encouraged by our isolation of small amounts of 7-bromotriazolopyridines we sought a brominating agent which was less reactive in electrophilic ring opening. Treatment of the 7-lithio-3-methyltriazolopyridine with NBS gave no bromination. Addition of DBTCE, to a solution of the lithio derivative in THF, gave the 7-bromo derivative in 25% yield; replacing this solvent by toluene increased the yield to 70–80%.

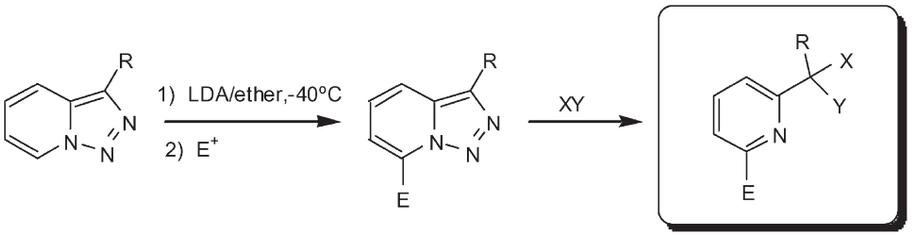


FIGURE 3

Once we had established a procedure for an efficient synthesis of the 7-bromo derivatives **7**, we studied the introduction of the nucleophiles. Most of the substitution reactions have been done with the 3-methyl-7-bromo derivative, because a substituent at position 3 allows greater stability in the products. Bromotriazolopyridines reacted with sodium methoxide, ethoxide or *n*-propoxide, in the appropiate alcohol at its boiling point, to give the corresponding 7-substituted triazolopyridines. Sodium phenoxide, sodium 4-methoxyphenoxide and sodium thiophenoxide, all in DMF at 90°C, afforded the corresponding derivatives. Boiling ethanolic solutions of piperidine or hydrazine converted the bromide into the 7-piperidino derivative and the 7-triazolopyridyl-hydrazine, in lower but acceptable (<60%) yield. No substitution was achieved using the bromo compound with azide ion, or with potassium isothiocyanate. We used selenium dioxide in boiling chlorobenzene, glacial acetic acid or sulphuric acid, to get the new disubstituted pyridines **8** (Figure 4).[13,14]

We were able to synthesize also 5- and 6-bromotriazolopyridines **9** and **10**, by more difficult routes, using Jones' methods,[15] and we studied their behaviour with nucleophiles. The bromo compound **9** reacted with sodium methoxide, sodium *p*-methoxyphenoxide, piperidine or morpholine to give 5-substituted triazolopyridines. The 6-bromo derivative **10** proved to be completely inert to sodium methoxide in methanol with no traces of methoxy compound after 95 hours at the boiling point (Figure 4).[15]

While extrapolation of pyridine's properties to predict reactivity in triazolopyridines is often risky, the reactions of 5-, 6-, and 7-bromotriazolopyridines do show the expected activation towards nucleophilic substitution at position 5 and 7, and benzenoid inertness at position 6.

The 7-substituted compounds can be considered as aza analogues of some 7-substituted indazoles that Professor Sylvain Rault, from Caen University (France), has studied as NO synthase inhibitors.[16] He has shown interest in our compounds and is now testing some of them in this respect.

HYDROGENATION REACTIONS

The parent compound **1a** was easily hydrogenated giving tetrahydrotriazolopyridine **11a** in high yield. When the triazolopyridine has a methyl group as substituent, the success of the hydrogenation reaction strongly depends on the position of the substituent. If the methyl group is at C3, compound **1b**, the reduction reaction gives **11b** in quantitative yield, however, when the methyl group is at C4 (**1c**) or C7 (**1d**), no hydrogenated products were observed and starting materials were recovered. If the substituent is an alkenyl group, the results also depends on its position. When at position 3 like in **1e**, the hydrogenation gives compound **11e**, but if it

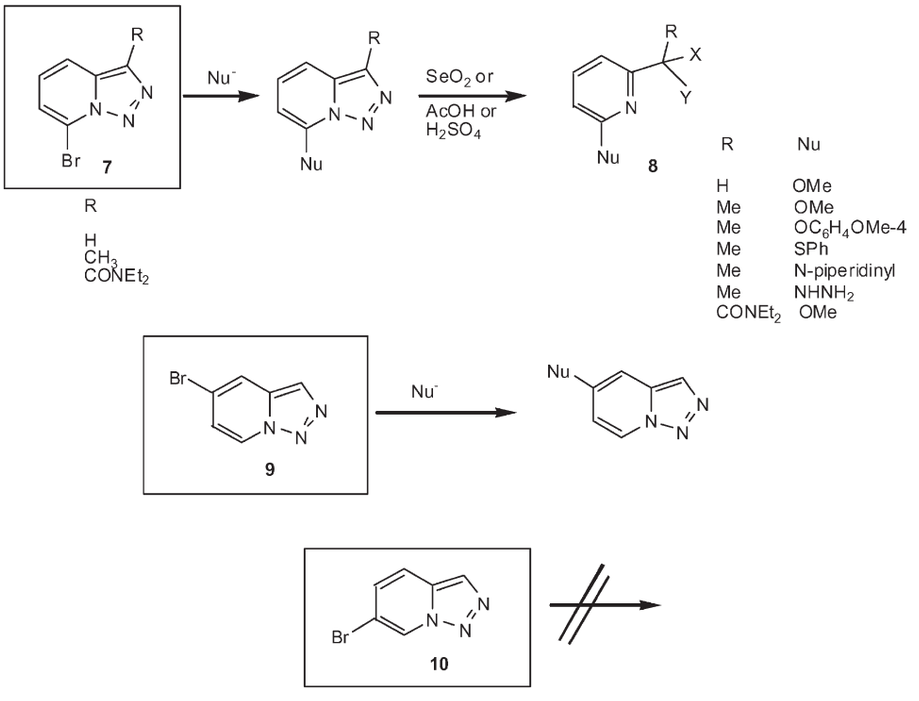


FIGURE 4

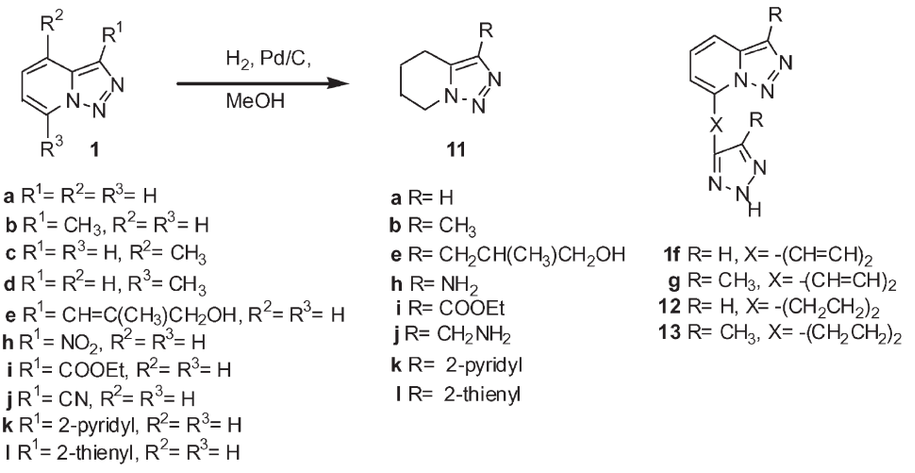
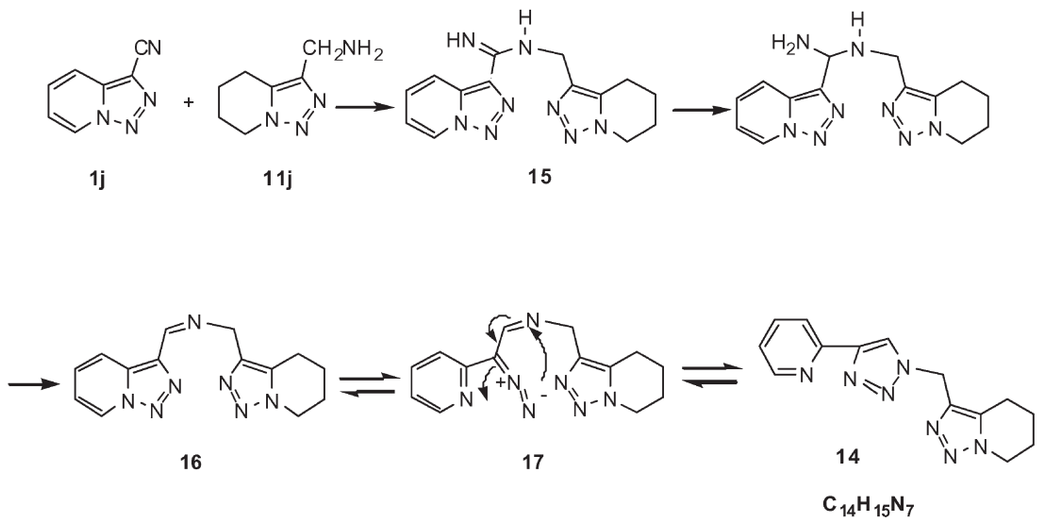


FIGURE 5

is in position 7, the reduction of the double bond is the only observed reaction; for example, compounds **1f** and **1g**, give **12** and **13** respectively. Under the used conditions, the alkyl and alkenyl substituents inhibit the reduction on the pyridine ring.[17]

With electron withdrawing substituents in the triazole ring, compounds **1h**–**k**, hydrogenation gives the corresponding tetrahydro derivatives, but the much lower reactivity of these compounds was reflected in much longer reaction times, and compounds **11h**–**k** were obtained only in moderate yields. In the case of an electron donor group as substituent, compound **1l**, no reaction was observed under standard conditions. Using double the amount of the catalyst and a reaction time six times longer, a small amount of hydrogenated compound **11l** was obtained (Figure 5).

In the case of the hydrogenation reaction of compound **1j**, two products were isolated. As well as 3-aminomethyltetrahydrotriazolopyridine **11j**, formed by reduction of the pyridine ring and the nitrile group, a surprising new compound was isolated. This compound shows a molecular formula of $C_{14}H_{15}N_7$. A careful study of its ^1H and ^{13}C NMR spectral data lead us to propose structure **14** for this compound, which can be formed as summarized in Scheme 2. A nucleophilic addition of **11j** to the starting material **1j** gives the imine intermediate **15** which is further hydrogenated, losing ammonia to give triazolopyridineimine **16** in equilibrium with the diazo tautomer **17**. This intermediate may undergo a new ring-chain tautomerism, giving a 1,4-disubstituted-1,2,3-triazole. This type of rearrangement had no precedent in the chemistry of [1,2,3]triazolo[1,5-*a*]pyridines.[17]



SCHEME 2

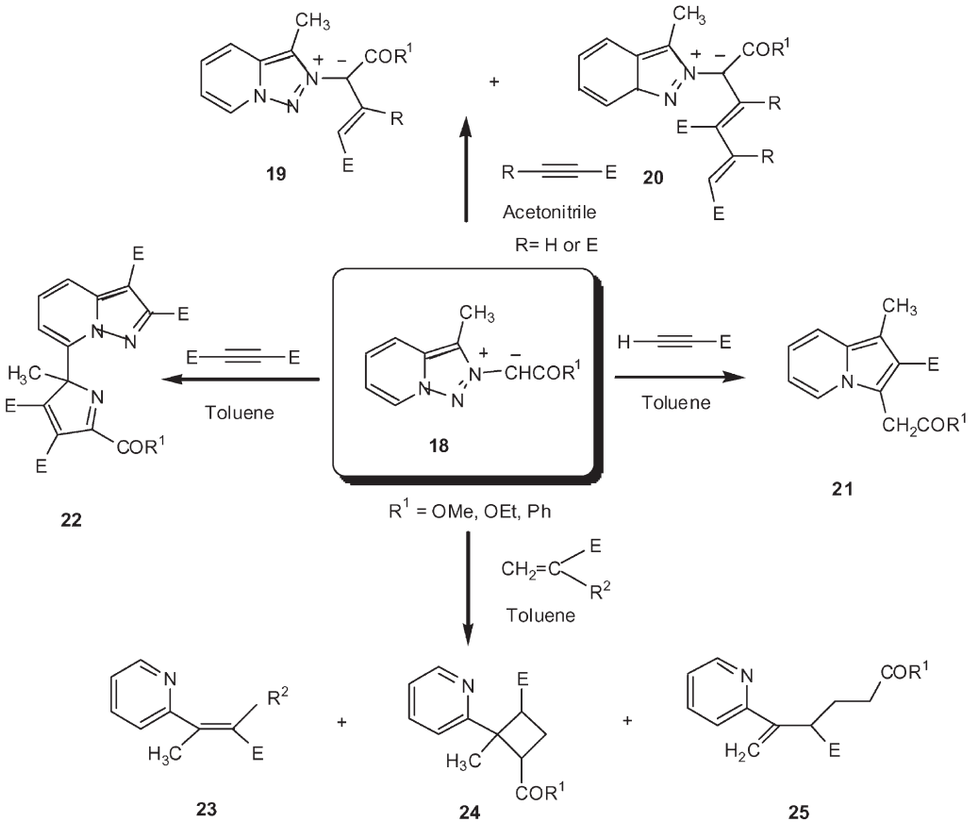


FIGURE 6

TRIAZOLOPYRIDINIUM YLIDES. SYNTHESIS AND REACTIVITY

An interesting synthesis of heterocyclic compounds is based on 1,3-dipolar addition to nitrogen ylides. We considered the possibility of synthesizing new tricyclic compounds from triazolopyridinium ylides, using acetylenic esters as 1.3-dipolarophiles. Unstable triazolopyridinium ylides of type **18** were prepared *in situ* from triazolopyridinium salts, when treated in acetonitrile with sodium carbonate. These ylides reacted with acetylenic esters to give yellow or orange compounds identified as new stable disubstituted ylides of type **19** and **20**, rather than a tricyclic compound.[18] This reaction is influenced by the nature of the solvent. A change of solvent to toluene produced completely different products; with methyl propiolate, indolizines **21** were formed

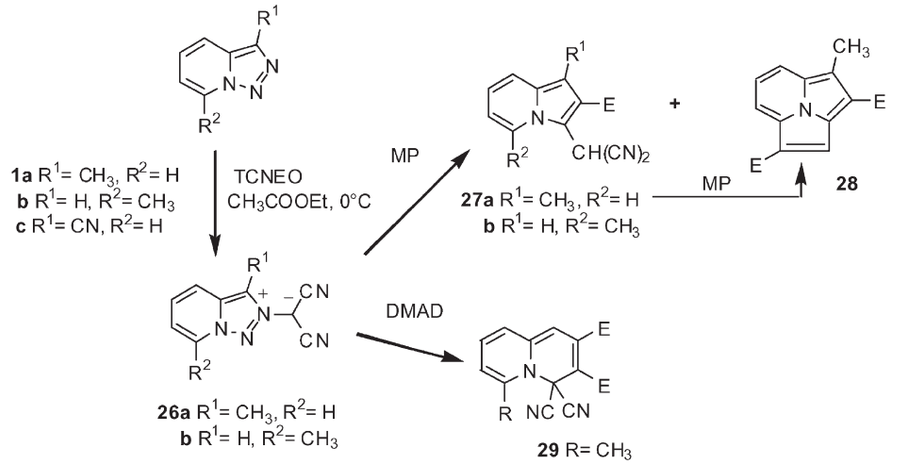


FIGURE 7

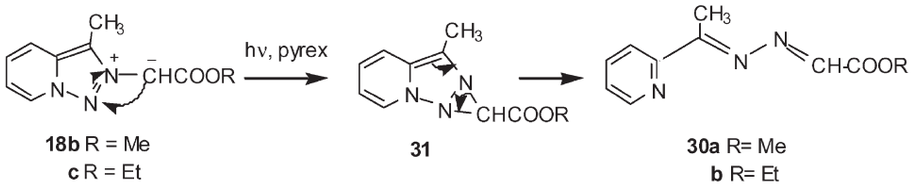


FIGURE 8

in high yield[19] and with dimethyl acetylenedicarboxylate, unexpected compounds whose structure was established, by an X-ray diffraction study, as pyrroleninylpyrazolo[5,1-*a*]pyridines **22**.[20] When the co-reagent was methyl acrylate in toluene, again the results were different, and a mixture of three compounds was formed in the reaction with ylide **18a**.[21] The major two compounds were pyridyl derivatives the 3-(2-pyridyl)acrylate **23** and the 3-(2-pyridyl)cyclobutane **24**. The relative stereochemistry about C2, C3, and C4 was established by DIFNOE experiments. The third isolated compound was the alkene **25**. Similar results were found with different ylides and methacrylates (Figure 6).[21]

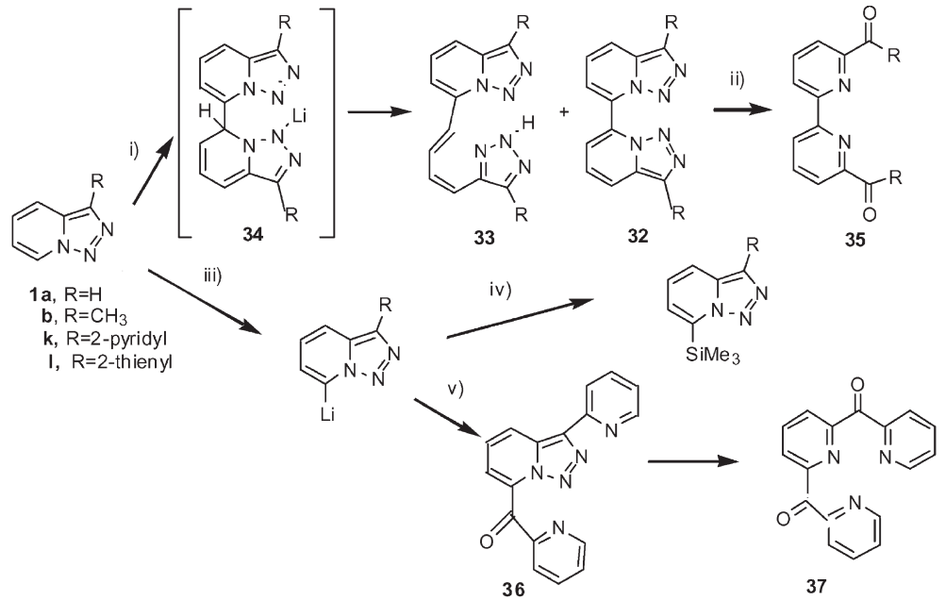
A mechanistic explanation was proposed to account for these three different modes of reaction between triazolopyridinium ylides and dipolarophile esters.[18–21]

We have also done studies of the reactivity of the stable dicyanomethylides **26** with acetylenic esters. The ylides were prepared by the method of Linn *et al.*[22] for reaction with TCNEO in ethyl acetate at 0°C. They exhibit very interesting spectroscopical data; we found again different results depending on the acetylenic ester used. The reaction with methyl propiolate (MP) gave two types of compounds, indolizines **27** and [2,2,3]cyclazines **28** from a classical [8 + 2] reaction of the indolizines and MP. In the case of reaction with DMAD, the ylide **26a** gave a new type of compound, the 4*H*-quinolizine **29**. We have proposed mechanistic explanations for the results found (Figure 7).[23]

PHOTOCHEMISTRY OF TRIAZOLOPYRIDINIUM YLIDES

The photochemistry of cycloimmonium ylides is a topic that has received considerable attention. Nevertheless, to the best of our knowledge, there have been no studies on the photochemistry of triazolopyridinium ylides. We present here our results on the photoreactions of some of these compounds.

Photochemistry of triazolopyridinium ylides **26a**,**b** and **18a–c** was studied. The photoreaction of



i) LDA, THF, -70°C, ii) H_2SO_4, H_2O, 95°C, or SeO_2 or AcOH

iii), LDA, THF, -40°C, iv) $ClSiMe_3$, v) PyCHO

FIGURE 9

dicyanomethylides **26a** and **26b**, results in the cleavage of the N^+-C^- ylide bond with formation of the parent heterocycles **1**, and probably the corresponding disubstituted carbene. When the unstable monosubstituted benzoylmethyltriazolopyridinium ylide **18a** was irradiated, a similar result was found and compound **1a** was isolated. Furthermore a mixture of two side products was isolated whose formation can be explained by invoking the corresponding carbene. Different results were found when the substituent in the ylide was a methoxy- or ethoxycarbonyl group; alkylidene hydrazones **30** were formed (Figure 8). To account for the formation of these open-chain isomers we proposed a photochemical electrocyclic reaction. This process involves four π-electrons, in a 1,3-dipolar species, forming a transient diaziridine **31**. Photochemical reactions of these ylides with MP and DMAD were also studied. The products obtained are similar to those found in the thermal reactions, but are produced in different solvents, reaction times, temperatures and with different yields.[24]

A NEW WAY TO 2,2′-BIPYRIDINES. A FACILE ROUTE TO NEW POTENTIAL HELICATING LIGANDS

While, as described previously, the usual reaction between triazolopyridines and lithium reagents gives a 7-lithio derivative, trapped by electrophiles, we have discovered more recently that the reaction is temperature dependent and at −70°C, in THF as solvent, a new reaction occurs, giving two major products: the 7,7′-bitriazolopyridines **32** and the butadienes **33**. The formation of these two compounds could be explained by a nucleophilic attack of the anion at the most reactive C7 of the starting material, to form the intermediate **34**, and this can undergo a six membered ring opening to give **33** or loss of hydrogen to give **32**.[15] We have some evidence of the formation of the intermediate **34**. As simple triazolopyridines, the bitriazolopyridines reacted with electrophiles to produce 2,2′-bipyridines **35**. Thus we have discovered a general route to 2,2′-bipyridines with a variety of substituents in the 6 and 6′ positions (Figure 9).[25] These compounds could be used in supramolecular chemistry because of their great complexing power for metal ions and in particular 2,2′-disubstituted-6,6′-bipyridines are useful building blocks for oligo-(bipyridines) which spontaneously form helical metal complexes.[26]

The synthetic chemical mimicry of the double-helix structural motif is an interesting area of research with intense activity in recent years. The formation of helicates and helices incorporating metal ions has become an important synthetic tool. Oligopyridines and related compounds are very useful helicating ligands. We consider that our discovery of a new route to 6,6′-disubstituted-2,2′-bipyridines **35** from triazolopyridine **1** could generate ligands which could form helicates. With this methodology, we have synthesized compounds like **32k**,**l** and **35k**,**l** from 3-pyridyltriazolopyridine and 3-thienyltriazolo-pyridine.[25] Also at −40°C we have synthesized compounds **36** and **37**. Potentially, compound **36** could be used to prepare new quatertriazolopyridines. This is the challenge that we have now in mind, to prepare new potential helicating ligands that should be able to form polynuclear complexes with numerous metal ions, not only with pyridines as substituents but also with other heterocycles like thiophenes, imidazoles or pyrazoles.

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