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TRIS-AZA-COPE REARRANGEMENT OF BICYCLIC N-CYANO-N'-VINYL OR N'-ARYLHYDRAZINES TO IMIDAZOLO-DIAZEPINE DERIVATIVES[#]

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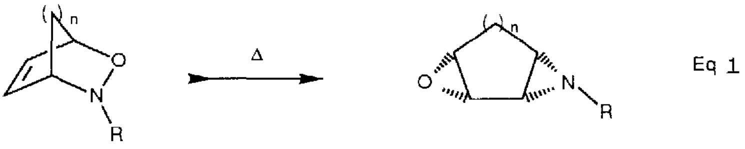
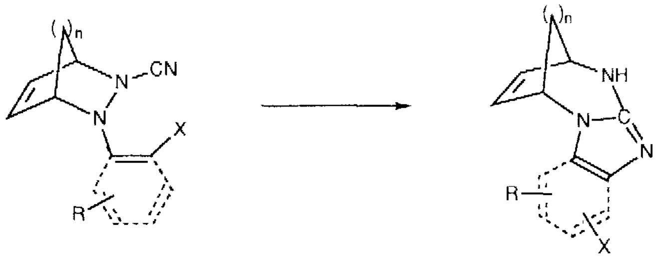
Abstracts *The bicyclic N-cyanohydrazines 6 and 12 undergo smoothly an unusual isomerisation to the new imidazolo-diazepines 9 and 15 The X-ray analysis of structure 9b is reported.*

The stereoselective "epoxyepimine" reaction has been established in our laboratory starting from suitably substituted bicyclic oxazines For instance, trichlorovinyl[1], 2,4,6-trichlorophenyl[2] as well as the captodative β-cyano-β-tert-butylvinyl[3] groups, which render the N-O bond proradical and labile, have been applied successfully as N-substituents (Eq 1)



(n = 1,2 or 3)

Our attempts to extend the rearrangement to bicyclic hydrazines led us to examine the reactivity of N-cyanodiazines 1 which are characterised further by either a captodative N'-vinyl or a N'-aryl substituent However, instead of bis epimination, we found that these diazines 1 undergo a rearrangement leading to new tri-respectively,tetra-cyclic imidazoles in good yields

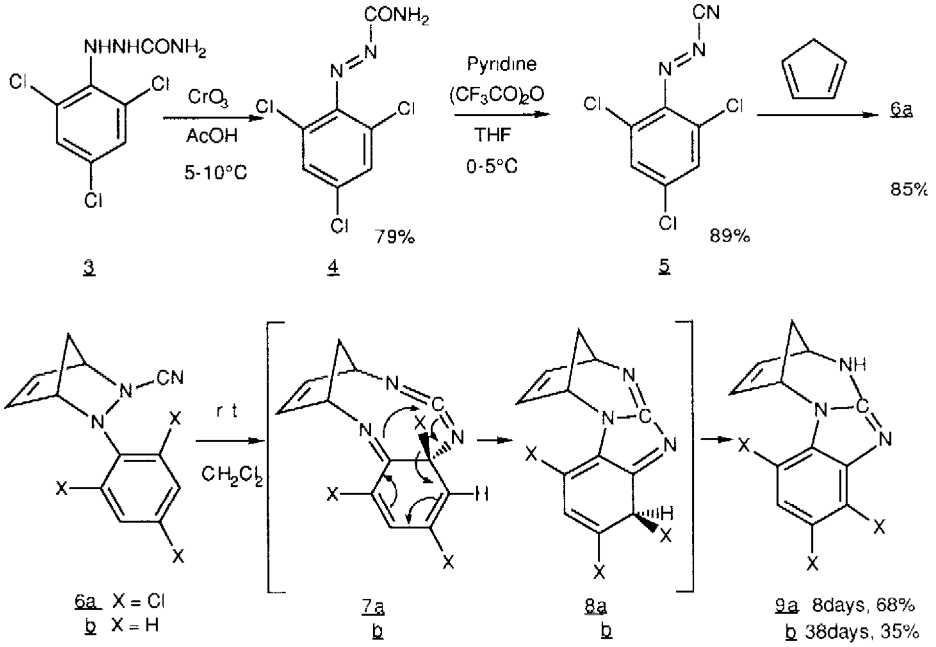


(n =1 or 2)

1 2

[#] Dedicated to Prof. E Weiss on the occasion of his 65th birthday

Thus with the 2,4,6-trichlorobenzenediazocyanide 5, which we made available[4] via the method depicted in scheme 1, we have obtained the unstable Diels-Alder adduct 6a A slow rearrangement to the tetracyclic amino-2-benzimidazole 9a is observed at room temperature, whereas on heating, retro Diels-Alder and other competitive reactions lead to complex mixtures With benzenediazocyanide, a similar result is obtained. Scheme 1 explains our title reaction by first a tris-aza-Cope rearrangement of 6 to the tetracyclic carbodiimide 7 The latter then would cyclise to 8 before a hydrogen shift produces aromatisation to 9.



-Scheme 1-

The easier isomerisation of 6a compared to 6b indicates steric and electronic substituent effects which are under study now.

The structure of 9b has been determined by X-ray analysis[8] (fig.1) and that of 9a follows from the similarity of its spectral characteristics to those of 9b

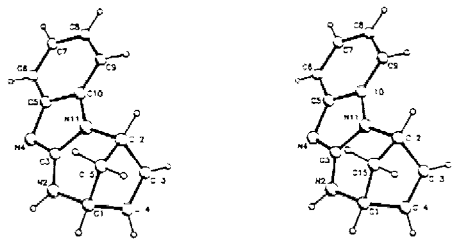
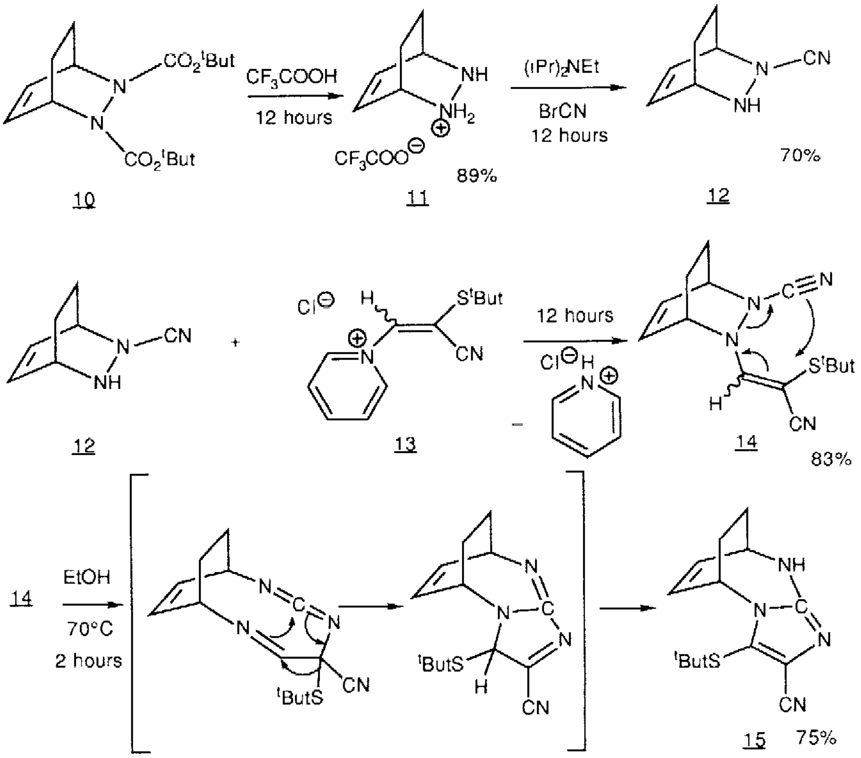


Fig 1 Stereoscopic view of the molecule 9b[12] .

As for the epoxyepimination reaction, the captodative N-vinyl substituent is of particular interest. Thus, in a second approach , we start from the easily available cycloadduct 10 (scheme 2) After hydrolysis to 11 and cyanation to 12, N-substitution with the pyridinium salt 13 produces 14 It smoothly undergoes the isomerisation sequence presented in scheme 2. The structure of 15 is based on NMR analysis and proved by X-ray analysis[9] .



-Scheme 2-

The reported new synthesis is based in its first step on a seldom encountered Cope rearrangement involving cyano groups. Pioneering work reported by Pellizzari[10] in 1918 and later by Bird[11] involves tricyano phenylhydrazine, aryl-cyanodiazetidinone and cyano-arylpyrrazolone rearrangements.

This promissing rearrangement is currently investigated and will be covered in a detailed publication

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[4] When the 2,4,6-Trichlorophenyldiazocyanide[5] <u>6a</u> (N-2,4,6-Trichlorophenyl-N'-cyanodiazene) is prepared via one of the two general methods[6,7], the product is obtained only in traces

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[8] The crystallographic data are as follows $C_{12}H_{11}N_3$, Mr=197 24, monoclinic, $P2_1/c$, a=9 848(3), b=9.642(3), c=11 120(4)Å, β=107,66(3)°, v=1006 1(6)Å^3, Dx=1 30g.cm^{-3} for Z=4 The intensities of 1969 h k±l independent reflections were collected on a Huber four circle diffractometer using MoKα graphite monochromatized radiation (λ=0 71069Å). 1351 reflections with I> 2 5 σ(I) were used in the refinement The structure was solved by SHELXS-86[13] and refined by anisotropic least squares on F values using SHELX-76[14] All H atoms were located from a difference Fourier synthesis and included in the refinement with a common isotropic temperature factor $w=1/(\sigma^2+0.00010F^2)$, S=1.80, R=0.039, wR=0.038 for 1351 observed reflections The list of atomic coordinates and molecular dimensions has been deposited with the Cambridge Data Center.
All the atoms but the hydrogens are located in four planes (max deviations from the mean planes less than 0.025 Å). A = C3, N4, C5, C6, C7, C8, C9, C10, N11; B = C1, N2, C3, N11, C12; C = C1, C12, C15 and D = C1, C12, C13, C14 The dihedral angles between these planes are A/B = 2° B/C = 64°, B/D = 71° and C/D = 135° There is a hydrogen bond between H-N(2) and N4 ; N2---N4 = 2.917(3) Å , H2---N4 = 2.01(2)Å (N4. 2-x, -y, 1-z).

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