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X=Y-ZH SYSTEMS AS POTENTIAL 1,3-DIPOLES.

1,5-ELECTROCYCLISATIONS OF IMINES

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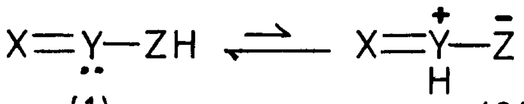
Summary. The naphthylidene imine of methyl (1-cyclopentenyl)glycine undergoes competitive double bond isomerisation and 1,5-electrocyclisation via a dipolar tautomer.

There has been much recent interest in 1,5-electrocyclisation processes[1-3] of dipolar systems and the cyclisation of even more extended dipolar systems has been reported.[4] Our recent discovery of the facile thermal tautomeric equilibration of X=Y-ZH systems with their 1,3-dipolar tautomers (1 ⇌ 2)[5] prompted us to explore the possibility of generating 1,5-dipolar species in this way.



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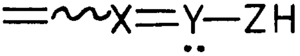

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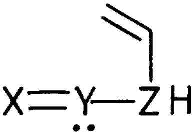
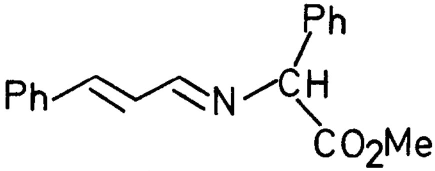


(4)

There are two types of vinylogous X=Y-ZH systems (3) and (4) capable of generating 1,5-dipolar species. Examples of both types of system have been prepared based on imines. However, the imines (5-7) analogous to (3) have unfavourable stereochemistry for cyclisation. Attempts to effect cyclisation of (5-7) by heating at 110° in toluene were unsuccessful. However, formation of the 1,5-dipole was demonstrated by trapping (toluene, 110°, 1h) with N-phenylmaleimide, e.g. (5)⟶(8; 79%) as a single stereoisomer.



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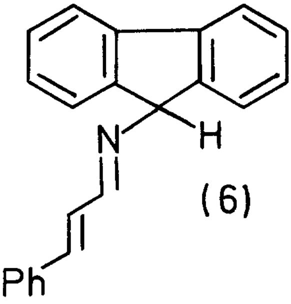

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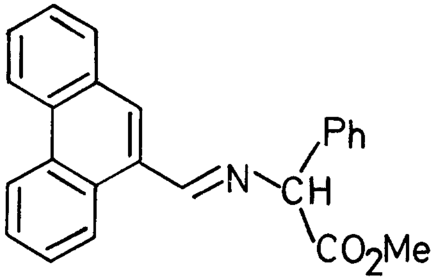

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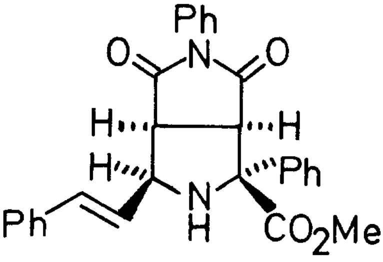


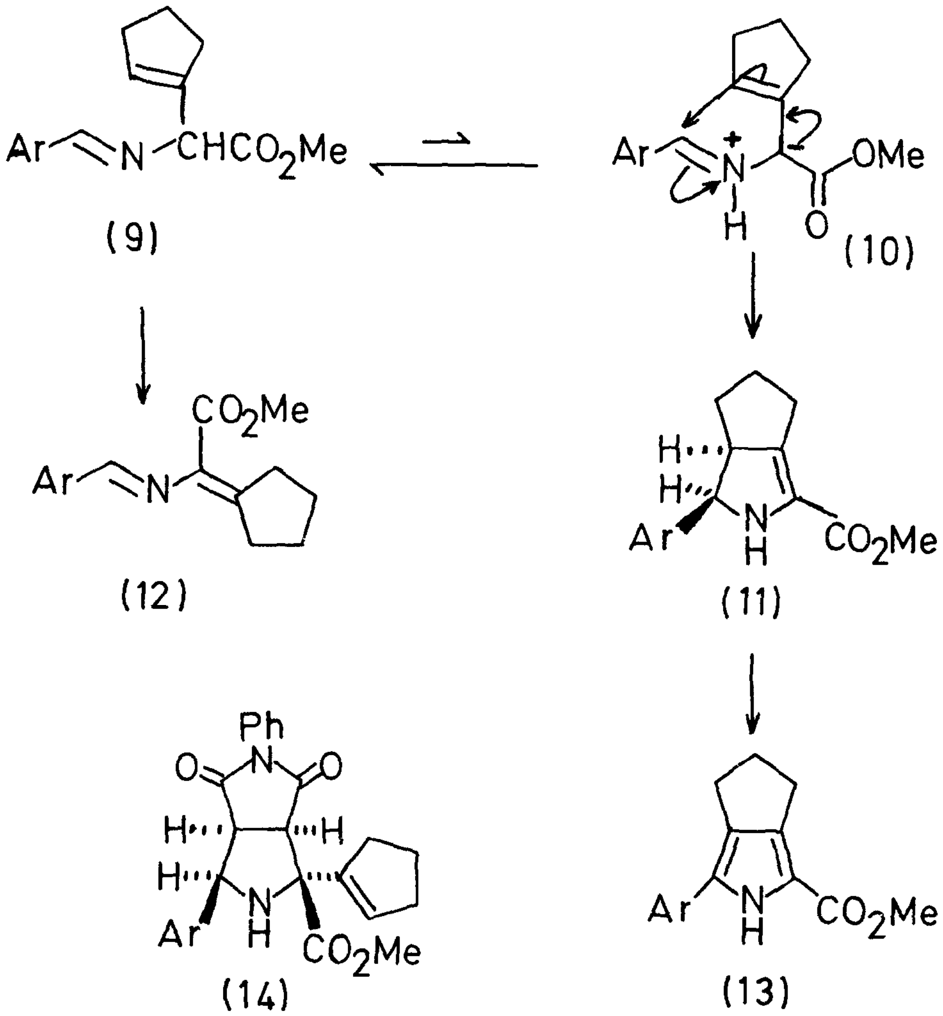
(8)

Table. Effect of solvent on competing 1,5-electrocyclisation and double bond migration of (9) at 80°.

Solvent	$t_{\frac{1}{2}}$(h)	Product Ratio (11)	:	(12)
CH_3CN	109	5.5		1
Xylene*	-	1.93		1
Toluene	43	1.2		1
Pyridine	5.7	1		24
DMF	3.7	1		32
Toluene/CH_3CO_2H	0.63	0		100
Toluene/DABCO	0.48	0		100

≠ Substrate concentration 0.137M

* Substrate concentration 0.4M, temperature 110°



Ar= 2-naphthyl

The imine (9) analogous to (4) was prepared from the corresponding β,γ-unsaturated α-amino acid[6] and naphthaldehyde. Stereospecific 1,5-electrocyclisation to (11) occurred on heating a solution of (9) in various solvents (Table). Concurrent double bond isomerisation (9⟶12) was observed and the ratio of (11): (12) was solvent dependent, with acetonitrile providing the best yield of (11). The addition of an equivalent of weak acid or base diverted the reaction to (12) (Table). The 1,5-electrocyclised product (11) was further characterised by oxidation (dry benzene, room temperature, 12h) to the pyrrole (13; 91%) with DDQ.

Formation of the 1,5-dipolar species (10) was demonstrated by trapping with N-phenylmaleimide (toluene, 110°C, 1h) to give (14; 88%).

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