AZADIENE ANALOGS AS SYNTHONS FOR HETEROCYCLES

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Azadienes, nitrogen analogs of butadienes, are expected to be effective starting materials for synthesis of nitrogen-containing heterocyclic compounds. However, 1- and 2-azabutadienes have not been so extensively utilized in heterocyclic synthesis. We previously reported the synthesis of substituted pyridines vis cycloaddition of 1-azabutadienes with enamines, which is one of rare examples of Diels-Alder reaction of 1-azadienes.

In this paper we studied reactions of azadiene analogs with several reagents which lead to formation of 3- to 6-membered heterocyclic compounds.

1. Oxidation

Oxidation of 1-tert-butyl-4-phenyl-1-azabutadiene (1a) with mCPBA in ether at room temperature for 3 h gave 2-tert-butyl-3-styryloxaziridine in 87% yield, while 1a was oxidized by H_2O_2 under basic condition to form an imidoyloxirane derivative (25% by nmr).

2. Reaction with Acid Chloride in the Presence of Triethylamine

In refluxing benzene phenylacetyl chloride was added to a mixture of the azadiene 1a and Et_3N and stirred for 7 h to afford 1-tert-butyl-3-phenyl-4-styrylazetidinone (45%, cis-isomer only). When Et_3N was added to a mixture of 1a and the acid chloride, the azetidinone (62%, cis : trans = 53 : 47) was obtained with 4% of 1-tert-butyl-3,4-diphenyl-2-pyridone.

3. Reaction with 1,3-Dipole

The azadiene 1a reacted with N-phenylbenzonitrilimine to give 1,3-diphenyl-4-tert-butyl-5-styryl-1,2,4-triazoline (56%) as the major product. On the contrary, a nitrilylide cycloadded to 1a across the C=C bond to afford a pyrrole aldehyde derivative (27%).

4. Reaction with Ester Enolate

Several 1-azadienes were reacted with enolates of substituted acetates in THF at room temperature for 20 h to form 3,4-dihydro-2-pyridone derivatives (27-78% yield). For example, 1-methyl-4-phenyl-1-azabutadiene and ethyl α-lithiopropionate gave 1,3-dimethyl-4-phenyl-3,4-dihydro-2-pyridone (54%) and its dehydrogenated 2-pyridone (15%). On the other hand, the reactions of an ester enolate with an 2-azadiene and with azines did not give 6-membered heterocycles but β-lactam derivative in fair to good yields.