A SIMPLE SYNTHESIS OF AZA[15]ANNULENES

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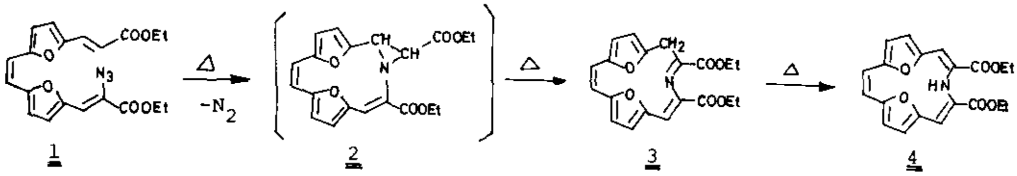
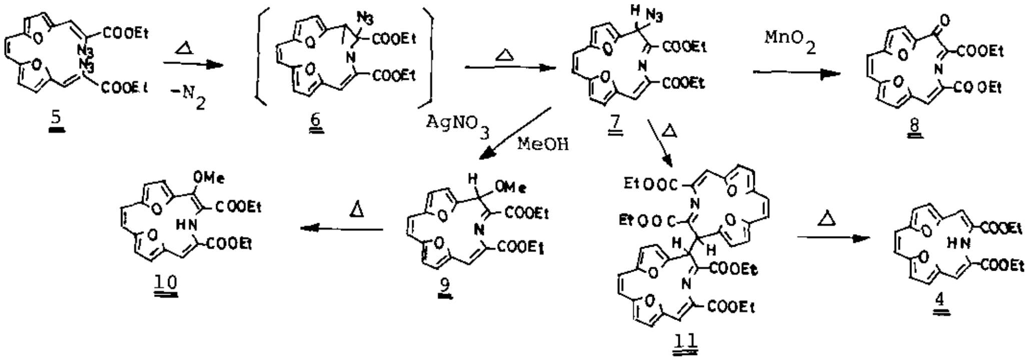
Aza[15]annulenes(4),(8),(10) were prepared via the thermolysis of the vinyl monoazido(1)and vinyl diazide (5).

The tautomerization of (3) into (4) could be monited by ^1H n.m.r. spectroscopy (in d_8-toluene at 75°).



Scheme 1

The thermolysis of vinyl diazide (5) led to (7),as an isolable reaction intermediate,from which 3-methoxy aza[15]annulene (10), 3-keto aza[15]annulene (8), and aza[15]annulene (4)were derived (Scheme 2).



Scheme 2

As expected, aza[15]annulenes (4)and(10)were proved to be strongly paratropic (16π),exhibiting NH proton at very low field, and outer olefinic protons at high field.