# SYNTHESIS OF OXYGEN-BRIDGED AZA[15]ANNULENE DERIVATIVES —NOVEL CYCLIZATION REACTION LEADING TO AZA-ANNULENE FRAMES—

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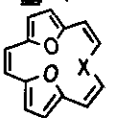
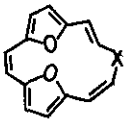
Previously, we prepared oxygen-bridged hetero[15]annulenes [1a (X= O, exists only as 1a) and 2a, 2b (X= S)], higher homologues of hetero-tropylidenes, and



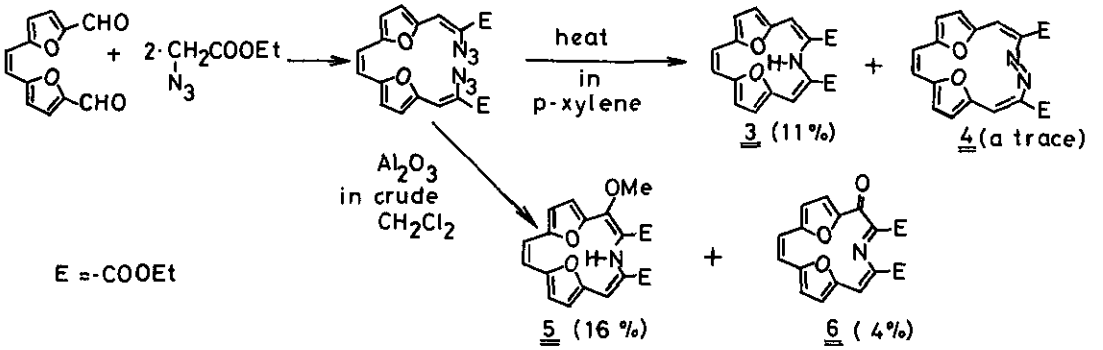
1a, X= O
2a, X= S



2b, X= S

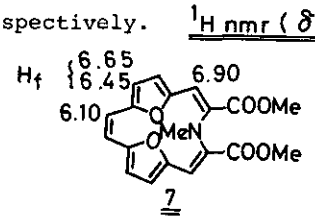
discussed their properties with respect to the heteroatom to be incorporated. The only missing group to be prepared was aza[15]annulene [X= NH or N-R], whose preparations have been so far unsuccessful except for one case (compound 7).

We now report that aza[15]annulenes 3 and 5 could be prepared according to following reaction scheme.




Present approach seems to have a wide applicablity, since the cyclization can be capable of proceeding against the considerable inside strain due to the presence of one inside hydrogen. Possible mechanisms of these reactions will be discussed.

These aza[15]annulenes were proved to be strongly paratropic (16π ), exhibiting each inside NH proton at very low field, and outer protons at high field, respectively. $^1$H nmr ( δ )

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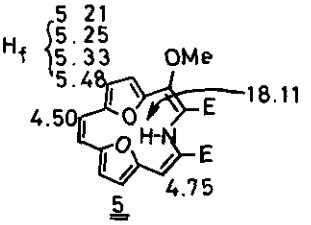


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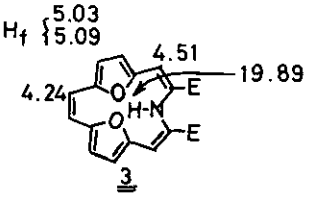


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