

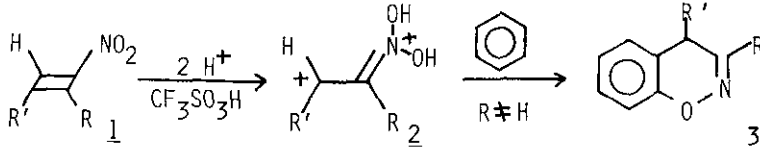
4H-1,2-BENZOXAZINES

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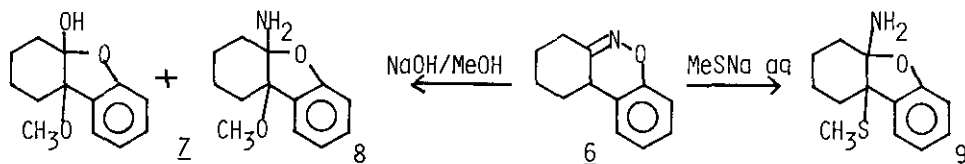
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In the course of our investigations concerning protonation of a nitro group in strongly acidic media, a novel synthetic method of 4H-1,2-benzoxazines was found. Diprotonation of 1-nitro olefins (1) in a super acid, trifluoromethanesulfonic acid (TFSA) yielded dications (2). In the presence of benzene, 2 ($R \neq H$) as a reactive electrophile react with benzene to give 4H-1,2-benzoxazines (3) in



moderate-good yields. Although the chemistry of 4H-1,2-benzoxazines seems to be concerned with that of well-known 1,2-benzisoxazoles, the former has not been studied. We examined reactions of solvolysis of 3,4-tetramethylene-4H-1,2-benzoxazine (6) which can be prepared from 1-nitrocyclohexene 4 in a quantitative yield.



Reflux of 6 in $NaOH-MeOH$ or in CH_3SnNa aq-dioxane yielded 7 & 8 or 9 respectively. Two plausible mechanisms for the reaction involve a N-O heterolytic cleavage. This reaction is regarded as nucleophilic addition of a nucleophile to the α -position of an oxime function which is chemically equivalent to a carbonyl group.