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NEW PERIPHERAL 1,3-DIPOLAR CYCLOADDITION REACTION

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An idea of peripheral 1,3-dipolar cycloaddition reaction was realized by the synthesis of anhydro 3H-pyrido[1,2,3-de]quinoxalinium hydroxide which was obtained from 8-aminoquinoline and α-bromoketone followed by deprotonation with triethylamine. The cycloaddition reaction of the above peripheral azomethine ylid was carried out with symmetrically substituted cis and trans olefin, asymmetrically substituted olefin, and acetylenic ester. Regio- and stereoselective cycloaddition reactions occurred in almost all cases. Thus, the endo [4+2] cycloadducts were obtained as single products indicating that the attractive interaction between the unsaturated moiety in the olefin and the conjugated π cloud in the ylid overwhelmed the steric repulsion. Two endo approaches are possible in the case of fumarate and actually two the [4+2] cycloadducts were formed. The regioselectivity was just as expected from polarized structure of the azomethine ylid and the olefin used. These [4+2] cycloadducts were readily dehydrogenated with chloranil or activated manganese dioxide giving the fully conjugated derivatives, indolizino[3,4,5,6-cde]quinoxalines, which were also obtained by the cycloaddition reaction of the peripheral ylid to acetylenic ester.