The sterically encumbered nitrone 1 adds cycloalkenes 2\(a-e\) at room temperature to form isoxazolo[2,3-\(a\)]-3\(H\)-indoles 3\(a-e\). These are, by action of traces of acid, rearranged to the 4,9a-methanobridged 1,5-benzoxazepines 5\(a-c-e\), while under more acidic conditions the alcohols 4 are finally formed. The latter may be dehydrated to the corresponding alkenes or rearranged to \(\omega\)-(3\(H\)-indol-2-yl)substituted aldehydes.

In a multistep photoinduced sequence compounds 5\(a-c-e\) (being linearly conjugated cyclohexadienimines!) are transformed into cyclopent[\(c\)]oxazocines 6\(a-c-e\). This sequence starts with an \(\alpha\)-cleavage of 5 and proceeds via a [2+2] cycloaddition, a [2+2] cycloreversion and a 1,5-\(H\)-migration to 6.

Being the exception among cycloalkenes 2\(a-e\), cyclohexene (2\(b\)) is added to 1 only very slowly, and the transformation of the adduct 3\(b\) into 5\(b\) was followed only spectroscopically. Details of all processes involved will be discussed.