FORMATION OF HETEROCYCLES BY INTRAMOLECULAR CYCLIZATION OF UNSATURATED CARBENIUM IONS

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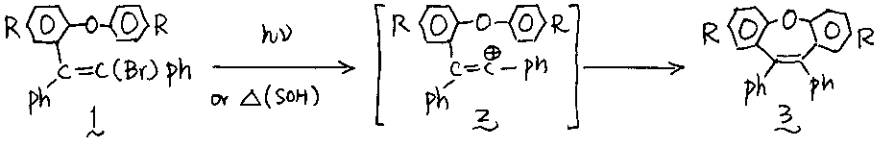
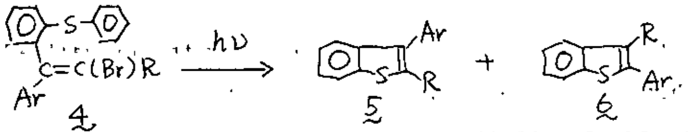
Intramolecular cyclization of vinyl bromides and allenyl chlorides bearing arylhetero groups was studied.

The reaction of β-(o-aryloxyphenyl)vinyl bromides 1 proceeded under both solvolytic and photolytic conditions. The products, dibenzoxepin derivatives 3, are derived from the resulting vinyl cations, followed by electrophilic attack on the aryloxyl group.



On the other hand, β-(o-arylthiophenyl)vinyl bromides 4 afforded benzothiophene derivatives 5 and 6 under photolytic conditions. Vinyl radicals and vinyl cations are responsible for the formation of 5 and 6, depending on the α substituent (R).



Intramolecular reaction of γ-(o-arylheterophenyl)allenyl chlorides 7 with $ZnCl_2$ or $SnCl_4$ gave six-membered heterocycles 8 as the sole products. Cyclization at the propargyl position on the allenyl cations is explained by the large positive charge density and the strain of the products derived from cyclization at the allenyl position.