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REACTIONS OF BENZOFURAN, BENZOTHIOPHENE AND INDOLES WITH PHOTOEXCITED DIBROMOMALEIC ANHYDRIDES

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Photoirradiation of dibromomaleic anhydride homologues in the presence of benzofuran, benzothiophene and indoles induces substitution and/or [2+2]cycloaddition. In either case, the reaction takes place at the 2- and/or 3-position of the above heterocyclic compounds. The reactive species is the photoexcited dibromomaleic anhydride homologues in the triplet state. Both the substitution and cycloaddition were observed with benzofuran and benzothiophene, while the substituted product alone was obtained in the case of indoles. The relative yield of the substituted product appears to be favored by the increase in donor-accepter interaction. In the case of benzothiophene-dibromomaleic anhydride system, energy of the activation of the substitution is higher than that of the cycloaddition by 1∿2 kcal/mol. A reaction mechanism involving a ^{3}exciplex is proposed, where the photosubstitution proceeds via more polar transition state than cycloaddition.