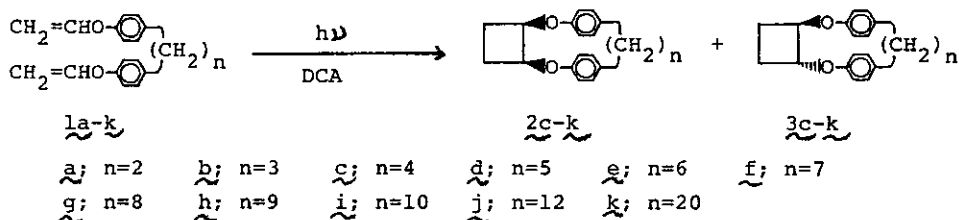


SYNTHESIS OF MACROCYCLIC POLYETHERS CONTAINING CYCLOBUTANE
RING BY INTRAMOLECULAR PHOTOCYCLOADDITION

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The intramolecular photocycloaddition between two vinyloxy groups were applied to the synthesis of macrocyclic polyethers containing cyclobutane ring, and the mechanistic features of these photoreactions were elucidated.

Irradiation of 1d-f in acetonitrile or benzene in the presence of 9,10-dicyanoanthracene (DCA) gave cis- and trans-cycloadducts, 2d-f and 3d-f, in good yields. The stereoselectivity in these photoreactions is influenced by solvent: In acetonitrile, the cis-cycloadducts 2 were predominantly produced via a photo-induced electron-transfer from 1 to ¹DCA*. In contrast, in benzene the trans-cycloadducts 3 were produced predominantly via intramolecular triplexes which are formed by interaction between 1 and ¹DCA*. Similar irradiation of 1c,g-k in acetonitrile gave the corresponding [2+2] cycloadducts 2c,g-k and 3c,g-k. However, no photoreaction occurred for 1a-b under similar conditions.



The photoreaction of 4a in benzene in the presence of 1,4-dicyanonaphthalene (DCN) gave selectively the trans-cycloadduct 6a in a 60% yield. From 4b-d, the corresponding cis- and trans-cycloadducts 5b-d and 6b-d were obtained in 2-3 : 1 ratios in 70-80% yields. In acetonitrile, these photocycloadditions occurred far less efficiently. The mechanisms of these photoreactions are discussed.

