SYNTHESIS OF MACROCYCLIC POLYETHERS CONTAINING CYCLOBUTANE RING BY INTRAMOLECULAR PHOTOCYCLOADDITION

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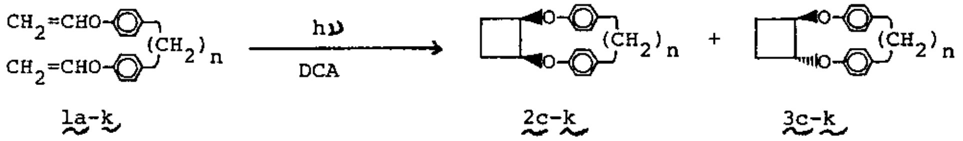
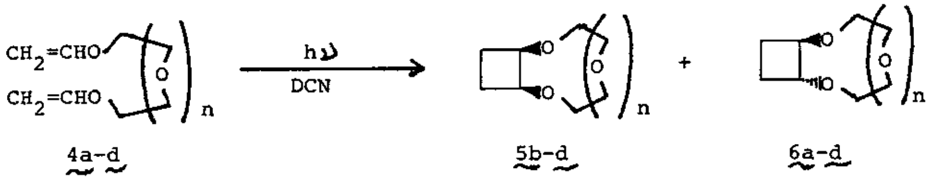
The intramolecular photocycloaddition between two vinyloxy groups were applied to the synthesis of macrocyclic polyethers containing cyclobutane ring, and the mechanistic features of these photoreactions were elucidated.

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 photoinduced electron-transfer from **1** to ^{1}DCA*. In contrast, in benzene the trans-cycloadducts **3** were produced predominantly via intramolecular triplexes which are formed by interaction between **1** and ^{1}DCA*. 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.



a; n=2 **b**; n=3 **c**; n=4 **d**; n=5 **e**; n=6 **f**; n=7
g; n=8 **h**; n=9 **i**; n=10 **j**; n=12 **k**; n=20

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.



a; n=1 **b**; n=2 **c**; n=3 **d**; n=4