Unexpected Photochemical Transformations of Dithienylacetylenes

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Dithienylethenes (DTE) undergo reversible isomerization to colored isomers upon light irradiation. These compounds are considered as one of the most promising classes of organic photochromic compounds due to outstanding thermal stability of both isomers and fatigue resistance. DTE are attractive for the design of hi-tech materials, including optical memory elements, molecular switches and for photopharmacology. Rational design and synthesis of DTE remain a challenging task because diverse practical applications require photoactive compounds possessing various properties. In this study, I report series of unexpected reactions connected with DTE. The first one was found during irradiation of DTE based on the cyclopropenone ethene bridge. It turned out that such DTE does not exhibit photochromic properties, but undergoes quantitative photoelimination of carbon monoxide upon UV-irradiation resulting in corresponding dithienylacetylene, which is widely used intermediate in preparation of photochromic DTE. The second part of my work is devoted to unprecedented dimerization of ethyl 4-thienyl-3-ketobutanoate under base conditions giving access to a new group of photochromic DTE bearing 4-hydroxycyclopentenone bridge. The third reaction was found in the case of DTE with thiophene and 2,5-dimethylthiophene substitutes, which possess an unexpected photochemical behavior. This compound do not show photochromic properties, but undergoes preparative photochemical rearrangement resulting in functionalized benzothiophene derivative. Reactions of this type were previously reported by our research group.

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