Exercises, Photochemistry 2021

May 5, 2021

Photochemistry of alkenes and polyenes

1. Explain why does irradiation of isomer *E*-40 with the light at 330 nm gives rise to a higher amount of isomer *Z*-40.

 

Chem. Commun. **2003**, 94–95.

2. Determine the composition of the photostationary state upon irradiation of a mixture of *cis*- i *trans*-stilbene isomers with a light at 313 nm. Molar absorption coefficients at 313 nm for cis is *ε* = 2400 dm3 mol-1 cm-1, and for trans *ε* = 16200 dm3 mol-1 cm-1. The quantum yield for isomerisation *cis* isomera to *trans* is 0.35, and for isomerization of *trans* to *cis* is 0.50.

A. Gilbert, P. Wagner, Essentials of Molecular Photochemistry, Blackwell Science 1991.

3. Explain why does the irradiation of a mixture of *trans*- and *cis*- *β*-ionol with triplet senzitizers with the triplet energy of *E*T ≈ 65 kcal/mol (such as benzophenone, *E*T ≈ 69 kcal/mol) under the conditions when the light is absorbed by the sensitizer only (350 nm) gives rise to the one way isomerization *trans*- to *cis*-.



*J. Am. Chem. Soc.* **1976**, *98*, 2935.

3. Explin the mechanism of photochemical *cis*-*trans* isomerization of *N*-methyl-4-(*β*-stiryl)piridinium salt in the presence of zinc cmplex with tetraphenylporphyrin (ZnTPP). For the elucidation of the mechanism take into account the following data: *E*T (ZnTPP) = 36.7 kcal/mol, *E*T (1) ≈ *E*T (2) ≈ 50 kcal/mol; *E*0 (ZnTPPox/ZnTPP) = 1.20 V.



G. J. Kavarnos, Fundamentals of Photoinduced Electron Transfer, VCH, New York, 1993.

*J. Org. Chem.* **1992**, *47*, 1409.

4. Photochemical isomerization of *trans*-stilbene to *cis*-stilben takes place in the presence of 9,10-dicianoanthracene as a sensitizer of electron transfer (photocatalyst), but the quantum yiled of the reaction is low. Suggest the mechanism of photochemical reaction taking into account the following data: *E*T (DCA) = 42 kcal/mol, *E*T (stilbene) = 49 kcal/mol, *E*0 (stilbeneox/stilbene) = 1.43 V vs. SCE , *E*0 (DCA/DCAred) = -0.98 V vs SCE.



*J. Phys. Chem.* **1984**, *88*, 2308.

5. Draw the structure of the photoproduct in the [1,3]-alkyl shift reaction.



6. Draw the structure of the photoproduct formed in the [1,5]- alkyl shift in the fllowing reaction:



*J. Am. Chem. Soc.* **1977**, *99*, 3507.

*Chem. Commun.* **1975**, 485.

7. Fill in the following reaction scheme:



*J. Chem. Soc. Chem. Commun.* **1974**, 183.

*Tetrahedron Lett.* **1976**, 3389.

8. On the following reaction scheme assign the photochemical and thermal processes taking into account the stereoselectivity of the thermal and photochemical pericyclic reactions.



*Chem. Ber.* **1975**, *108*, 1052.

9. Explain the formation of product with unexpected stereochemistry in the following photochemical reaction, taking into account the type of excited state involved, and the analysis of the frontier molecular orbitals.



*J. Am. Chem. Soc.* **1967**, *89*, 112.

10. Explain the mechanism of the following photochemical reactions.



*J. Am. Chem. Soc.* **1972**, *94*, 5504.



*J. Org. Chem.* **1976**, *41*, 3931.



11.In the following photochemical reactions draw structures of the oxa-di-π-methane or aza-di-π-methane rearrangements and explain the mechanisms of the reactions.



*J. Am. Chem. Soc.* **1966**, *88*, 1835.



Helv. Chim. Acta 1980, 63, 2434.



*J. Chem. Soc. Chem. Commun.* **1987**, 167.

12. Explain the mechanism for the formation of photoproducts.



*J. Am. Chem. Soc.* **1978**, *100*, 535.



*J. Org. Chem.*, **1993**, *58*, 6390.

13. Draw structures of photoproducts in the following reactions and explain the reaction mechanisms.



*Angew. Chem. Int. Ed.*, **1963**, *2*, 743.



*Zh. Org. Khim.* **1986**, *22*, 2464.



*J. Am. Chem. Soc.* **1966**, *88*, 3765.



*Chem. Ber.* **1964**, *97*, 2425.

14. Photochemical cyclodimerization with triplet sensitizers gives high yields of cyclopropane, cyclobutene, cyclopentene, cyclohexene and cycloheptene. Explain why the photochemical reaction of cyclooctene initiated by triplet sensitizers gives low yields of dimeric products.

15. Draw the structures of photoproducts in the following cycloaddition reactions and explain the mechanisms of their reactions. Why are the reactions regioselective?



16. Draw the structure of anticipated photoproduct, taking into account the steric factors.



17. Photochemical reaction of phenyl vinyl ether and ethyl vinyl ether in the presence of dicyanobenzene as a sensitizer in CH3CN gives two cyclobutane photoproducts. Draw the structure of photoproducts and explain the mechanism of their formation.



18. The irradiation of a mixture of 1,1-diphenylethene and 1,1-dimethylethene in the presence of dicyanobenzene leads to the formal (2π + 4 π) cycloaddition. Draw the structure of the product and explain the mechanism of its formation.

