

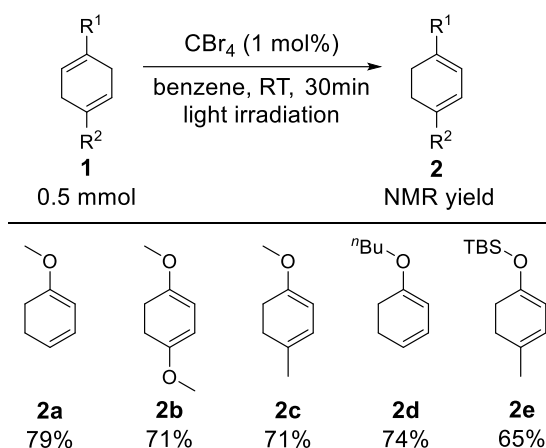
Utilization of HBr Generated by Photolysis of CBr₄: Development of Isomerization Reaction from 1,4-Cyclohexadienes to 1,3-Cyclohexadiens

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Keywords; Photolysis, Cyclohexadiene, Isomerization

Generation of hydrogen bromide (HBr) by photolysis of carbon tetrabromide (CBr₄) is a powerful method to use HBr under a dry organic solvent.¹ However, the use of 254 nm light irradiation is limited by the low transmittance of the light to general glassware and organic solvents. In this study, we found the photolysis of CBr₄ by irradiation of 365 nm light under general glassware and organic solvents. For the application of the photolysis of CBr₄, the isomerization reaction of moisture-sensitive 1,4-cyclohexadiene² was achieved by the catalysis of *in situ* generated HBr by photolysis of CBr₄ under the irradiation of 365 nm light.

1,4-Cyclohexadienes **1a–e** were stirred for 30 min in the presence of a catalytic amount (1 mol%) of CBr₄ under the irradiation of 365 nm light. After the reaction, the corresponding 1,3-cyclohexadienes **2a–e** were obtained in good yields. On the other hand, 1-methyl-1,4-cyclohexadiene and 1,4-cyclohexadiene, which do not contain oxygen atoms, were not reacted. We also investigated the detailed mechanism of the photolysis of CBr₄, *in situ* generation of HBr, and isomerization of 1,4-cyclohexadienes by theoretical calculations using the GRRM program.³



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