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PHOTOISOMERIZATION OF 6-METHYLBICYCLO[4.1.0]HEPTAN-2-ONES[1]

William G. Dauben and Williard M. Welch

Department of Chemistry, University of California
Berkeley, California 94720

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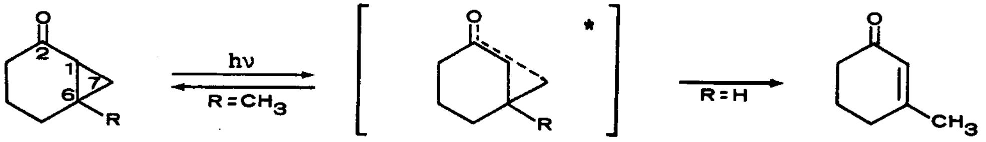
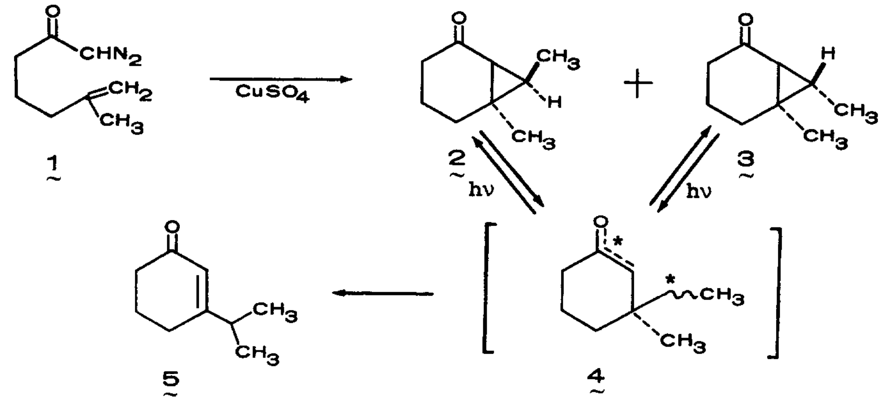
In the photoisomerization of a bicyclo[4.1.0]heptan-2-one to a 3-alkylcyclohex-2-en-1-one, it was found that the presence of an alkyl group at the 6-position inhibited the rearrangement.[2] Furthermore, it was found that alkyl groupings at the 7-position greatly increased the efficiency of the migration of the C-6 hydrogen atom. The effect of such C-7 substitution on the migration of a C-6 alkyl group has now been evaluated.

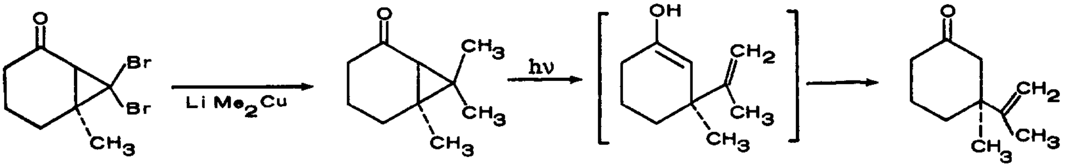


The starting ketones, endo- and exo-6,7-dimethylbicyclo[4.1.0]heptan-2-ones (**2** and **3**, respectively) were prepared by intramolecular ring closure of the unsaturated diazoketone **1**.[3] The two isomers formed in the reaction were separated by a combination of column chromatography and preparative vpc.



Irradiation (Corex) of each isomer in benzene first gave a mixture of both isomers showing that, indeed, the C-1:C-7 bond was opened to intermediate 4 and that the preferred reaction pathway of this species was ring closure back to 2 and 3.[4] Upon continued irradiation, 3-isopropylcyclohex-2-en-1-one (5) was the only rearrangement product formed. Thus, the presence of a substituent on C-7 increased the efficiency of the alkyl migration from C-6 to C-7 so that the process can compete with the stereoisomerization of C-7 since under these same irradiation conditions, 6-methylbicyclo[4.1.0]heptan-2-one was stable (less than 1% of the ketone reacted).

To further evaluate the effect of substituents at C-7 on the photorearrangement process, 6,7,7-trimethylbicyclo[4.1.0]heptan-2-one (7) was prepared by reaction of lithium dimethyl copper with 6-methyl-7,7-dibromobicyclo[4.1.0]-heptan-2-one (6).[5] Irradiation of 7 under the above conditions gave the unsaturated ketone 8 in 90% yield. This reaction product clearly results from a Norrish Type II hydrogen abstraction process. The γ-hydrogen abstraction from the endo methyl group in 7 as compared to the absence of such a reaction with the monosubstituted endo isomer 2 warrants further study.



6 7 8

The results obtained in this study clearly illustrate the delicate balance that exists between the many possible reaction routes available to a photo-excited cyclopropyl conjugated ketone. The substituent effects are of such importance that they can be used to control the type of photolytic ring opening such a chromophore undergoes.

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REFERENCES

1. This work was supported by PHS Grant No. 00709, National Institutes of Arthritis and Metabolic Diseases, U.S. Public Health Service.

2. W.G. Dauben, G.W. Shaffer, and E.J. Deviny, J. Amer. Chem. Soc., 92, 6273 (1970).

3. This material was prepared in the following manner: a benzene solution of methyl 5-oxohexanoate [N.F. Albertson, J. Amer. Chem. Soc., 70, 669 (1948)] was allowed to react with a salt-free hexane solution of ethylidenetriphenylphosphorane. The resulting ester was saponified, the dry sodium salt of the acid allowed to react with oxalyl chloride, and the resulting acid chloride converted to the diazoketone with diazomethane.

4. A similar efficient photo-epimerization has been reported for 4,5-diphenylbicyclo[3.1.0]hexan-2-one [H.E. Zimmerman, K.G. Hancock, and G.C. Licke, J. Amer. Chem. Soc., 90, 4892 (1968)].

5. The following synthetic procedure was followed: 3-methylcyclohex-2-en-1-ol was allowed to react with dibromocarbene (bromoform and potassium *t*-butoxide) in hexane, and the resulting dibromide mixed with lithium-dimethyl copper. The crude product was oxidized with Jones' reagent and the desired ketone obtained in 22% yield by a combination of column chromatography and preparative vpc.