

PHOTOISOMERIZATION OF 1-VINYL-7,7-DIMETHYL BICYCLO [2.2.1] HEPTA-2-ONE

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Abstract

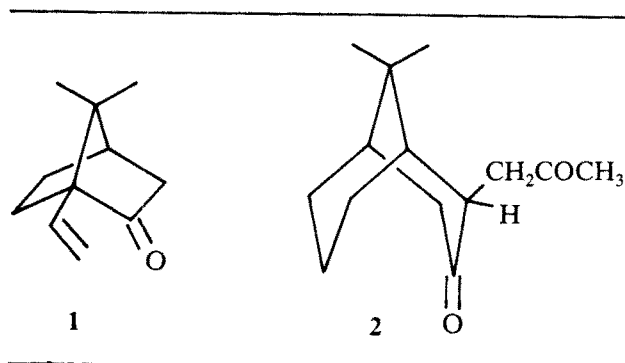
The acetone sensitized photolysis of the title compound gave 2-(2-oxopropyl)-9,9-dimethyl bicyclo [3.3.1]nona-3-one. A bridgehead cyclopropane intermediate was then suggested for the formation of the photoproduct.

Introduction

The photochemistry of bichromophoric β , γ -unsaturated ketones has been investigated extensively in the last two decades [1]. Studies on the spectroscopic properties of these compounds have shown immense differences from those of other unsaturated ketones [2]. These differences have been attributed to the interaction between the carbonyl group and the double bond which is dependent on the orientation of the two groups [3]. Direct irradiation of β , γ -unsaturated ketones generally leads to a 1,3-acyl shift, whereas triplet sensitization results in an oxa-di- π -methane rearrangement. In view of the wide interest in the photochemistry of β , γ -unsaturated ketones, we have studied the photolysis of 1-vinyl-7,7-dimethyl bicyclo [2.2.1] hepta-2-one [4] because its photoisomerizations, if any, was expected to result in bridgehead olefin and bridgehead cyclopropane under direct and sensitized irradiation conditions respectively.

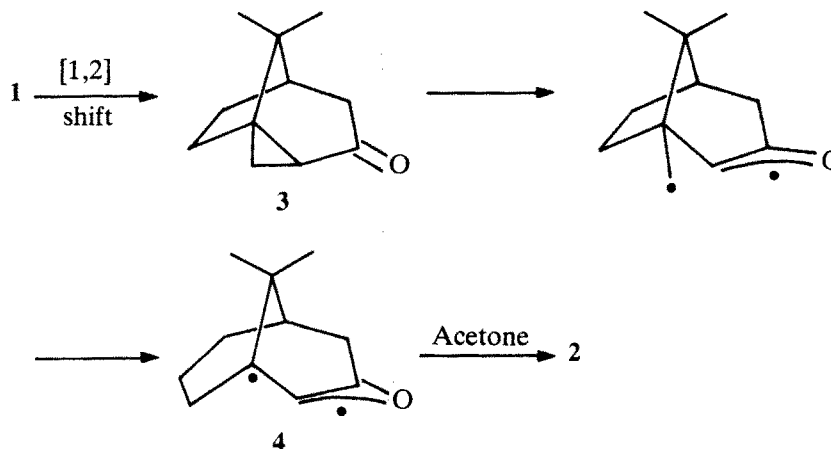
Results and Discussion

Irradiation of compound **1** in methylene chloride at 2537 Å for several hours showed no change. On the other hand, irradiation of 0.018 molar of this compound in acetone under nitrogen using a Hanovia low pressure



mercury lamp for 27 hours gave diketone **2** in 60% yield and an unidentified compound.

The identification of compound **2** was based on its spectroscopic data. The mass spectrum showed a molecular ion peak at 222. Its IR spectrum displayed two strong absorption bands at 1730 and 1700 cm^{-1} characteristic of the aliphatic and eight membered ring ketones respectively. The presence of these two carbonyl groups was further confirmed by the existence of two low field peaks at 190 and 196 ppm in its ^{13}C -NMR spectrum. The ^1H -NMR spectrum of **2** (δ , CDCl_3) showed peaks at 2.4 (m, 2H), 1.95-2.2 (m, 6H), 1.2-1.9, (m, 8H), 1.0 (s, 3H) and 0.9 (s, 3H). To clarify the spectrum, we took the NMR in the presence of the shift reagent trisdipivalomethanatoeuropium (III) dipyridine complex, $\text{EU}(\text{DPM})_3$ (0.05 mole). The spec-



trum showed that the downfield protons consisted of a multiplet (2H), a doublet ($J=13$ Hz, 2H), a sharp singlet (3H), and a triplet ($J=13$ Hz, 1H).

Our result demonstrates that compound 1 after excitation to a triplet state undergoes the oxa-di- π -methane rearrangement to 3. This photoproduct which is a α,β -cyclopropyl ketone is thought to transform into diketone 2 through the intermediate 4 under reaction conditions. Similar results of the phototransformation of 3 to 4 has been reported by Dauben and Welch in the case of exo and endo-6,7-dimethyl bicyclo[4.1.0]hepta-2-ones [5].

The result obtained in this study shows that although the bridgehead cyclopropane 3 could not be isolated because of the addition of acetone, this kind of reaction is to our knowledge, a novel example in the long time research of photochemistry of the unsaturated ketones.

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