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PHOTOCHEMICAL REACTIONS OF A BICYCLIC KETONE

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7,7-Dimethyl[3.2.0]bicyclohept-2-ene-6-one (I) (1) was photolyzed with a Hanau Q 81 mercury immersion lamp. When an inert solvent (cyclohexane) was used, only polymeric products were formed; however, in a 10-20% solution in methanol, I was converted quantitatively to two products. These products, present in approximately equal amounts, were partly separated by distillation through a spinning band column. Final purification of small samples was achieved by preparative vapour phase chromatography. Based on their elemental analyses, IR, UV and NMR spectra, the products were identified as the acetal IV and methyl 7-methyl-4.6-octadienoate V*.

Both products were hydrogenated catalytically (PtO_2, ethanol). Hydrogen uptake was consistent with the number of olefinic bonds present in each compound. Satisfactory

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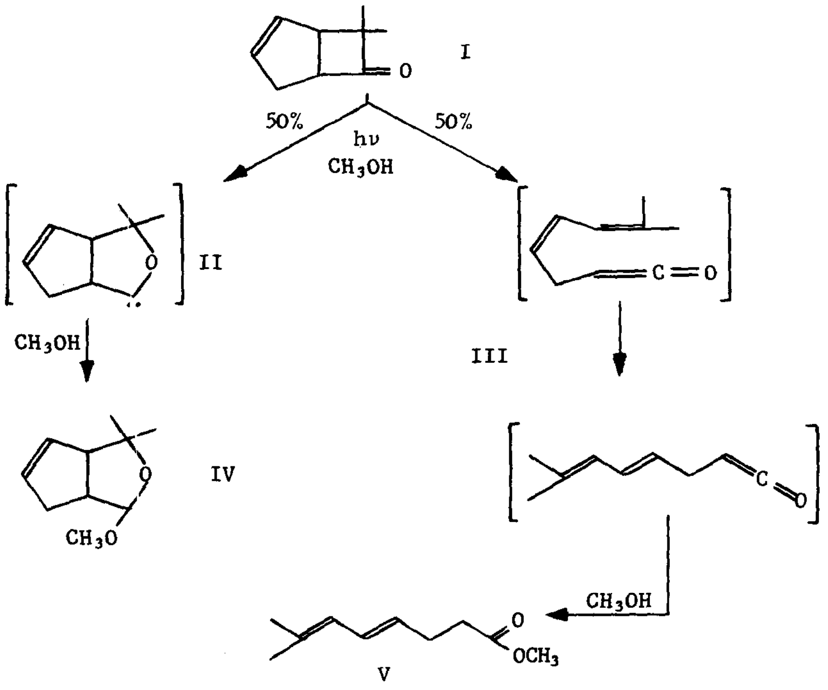
* IV: b.p.$_{733}$= 197°C (corr.), n_D^{20}= 1.4832, $\nu_{max}(CCl_4)$1195, 1100, 1050, 1010, 980, 935 and 825 cm^{-1}. The NMR spectrum (CCl_4, TMS as internal standard) consists of two singlets (two methyl groups) at 1.11 and 1.30 p.p.m., a complex multiplet (methylene and methin groups, intensity 4) between 2.3 and 3.1 p.p.m., a singlet (methoxy group) at 3.22 p.p.m., a doublet (acetal hydrogen, J = 1 cps) at 4.51 p.p.m. and a multiplet (two olefinic protons) centered at 5.56 p.p.m. Footnote continued on next page.



analyses were obtained and the IR and NMR spectra were in accord with the structures of the hydrogenated products.

Since the rings in I are fused cis, it is assumed that the cis configuration is still present in IV. In addition cis-trans isomers can be distinguished, depending on the configuration at the acetal carbon. From a Dreiding model it is seen that the dihedral angle between the acetal hydrogen and the

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V: b.p.$_{734}$= 224°C (corr.), n_D^{20} = 1.4824, λ_{max}(EtOH) = 236 mμ (ε25,750), ν_{max}(CCl_4) 1745, 1250, 1195 and 1162 cm^{-1}. The NMR spectrum (CCl_4) consists of a singlet (one methyl group) at 1.72 p.p.m., a doublet (one methyl group, J = 5 cps) at 1.76 p.p.m., a multiplet (two methylene groups) centered at 2.32 p.p.m., a singlet (methoxy group) at 3.60 p.p.m. and a multiplet (three olefinic protons). scattered from 5.0 to 6.3 p.p.m.

adjacent tertiary hydrogen is close to zero for the cis isomer and about 120° for the trans isomer. According to the Karplus-equation (2) the corresponding coupling constants for spin-spin interaction are 8 and 4 cps, respectively. The observed value of $J = 1$ cps ($J = 1.5$ cps when IV is hydrogenated) is evidence that the trans isomer was formed.

A similar photoreaction as the one leading to IV was only recently reported to take place with cyclocamphanone (3). The acetal formed in those experiments dimerized to the bis-acetal within a few days. No such dimerization was observed for IV, but it shows a slight tendency to decompose on prolonged storage. Whether a carbene type intermediate II is involved in the formation of IV, similar as suggested for cyclocamphanone (3), cannot be decided at present.

The type of reaction leading to V has many times been reported before (4) and is generally agreed to involve a ketene intermediate like III. The high value of the UV extinction coefficient ($\varepsilon = 25,750$) of the ester V is indicative of its trans configuration (5). Therefore cis-trans isomerization of the intermediate ketene must have occured.

Further work with I and similar ketones in various solvents is in progress.

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