

The Photolysis of 2,2,6,6-Tetramethyltetrahydropyran-3-one.

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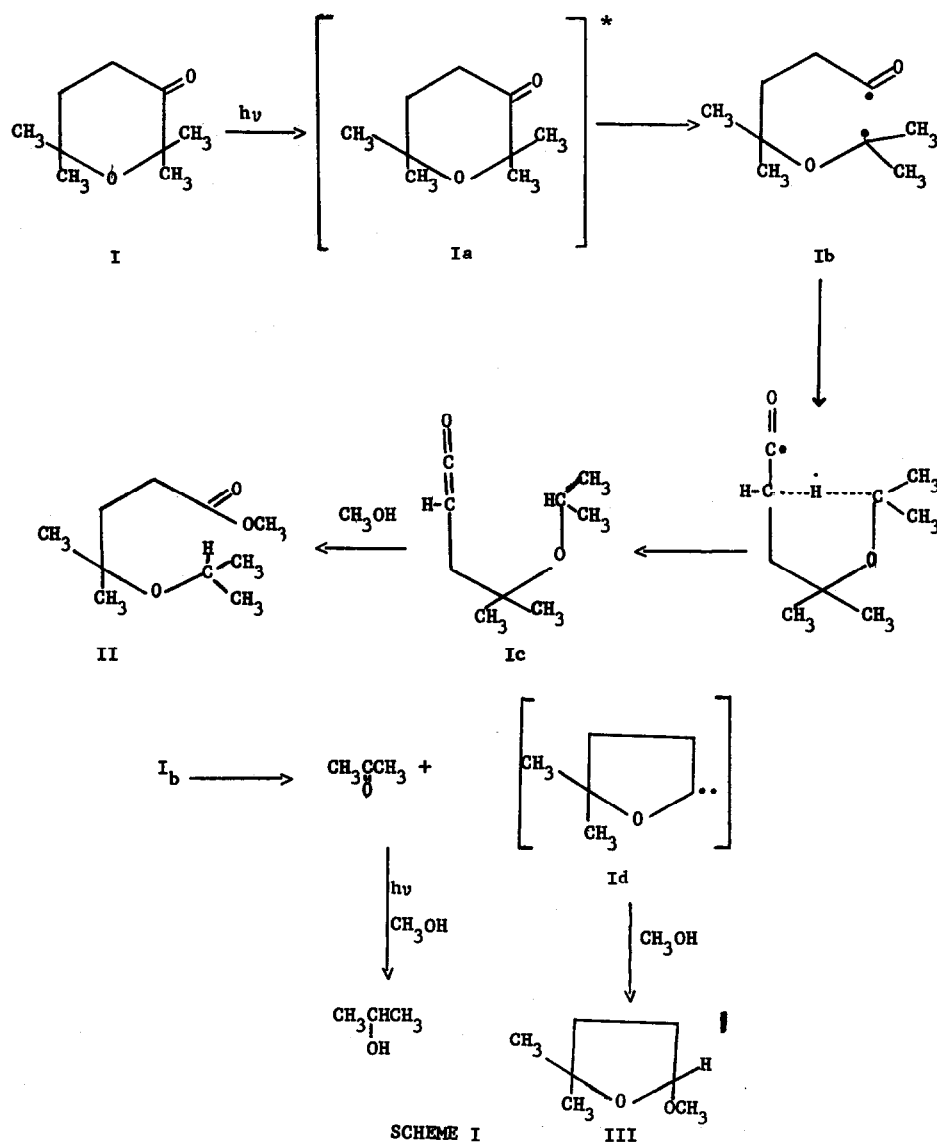
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During an investigation of the photolysis of oxacyclic ketones¹, we have studied the photolysis of 2,2,6,6-tetramethyltetrahydropyran-3-one (I) in methanol. The procedure of Korobitsyna and Pivnitskii² was used to synthesize I. Preparative gas chromatography yielded I in purity greater than 99.9%. When I (0.582g, 0.0037 mole) was dissolved in 10 ml of methanol and irradiated for 12 hrs with a high pressure mercury vapor lamp (450 W), the products isolated by gas chromatography were found to be: acetone, 7.1%, 2-propanol, methyl 4-isopropoxy-4-methyl-pentanoate (II), 55.4%, and 2,2-dimethyl-5-methoxytetrahydrofuran (III), 37.5%. An accurate yield of 2-propanol could not be determined. Acetone and 2-propanol were identified by comparison of their retention times with those of authentic samples at various oven temperatures. Methyl 4-isopropoxy-4-methylpentanoate (II) was identified by IR, NMR, and elemental analysis. The IR spectrum showed a very strong absorption at $\sqrt{\text{CCl}_4}$ 1738cm⁻¹ (ester C=O). The NMR spectrum (CCl₄) had absorptions at δ 1.06 (d, J=6 cps, 6H, H-C(CH₃)₂), 1.12 (s, 6H, -CH₃ at γ -C), 1.73 (m, 2H, β -C(H)), 2.27 (m, 2H, α -C(H)), 3.60 (s, 3H, -OCH₃), and 3.75 (septet, J=6cps, 1H, H-C(CH₃)₂). Anal. Calcd. for C₁₀H₂₀O₃: C, 63.80; H, 10.71. Found: C, 63.65; H, 10.55. 2,2-Dimethyl-5-methoxy-tetrahydrofuran (III) was identified by IR and NMR. The IR spectrum had absorptions at $\sqrt{\text{CCl}_4}$ 2824 cm⁻¹ (H-C-O), 1380 and 1367 cm⁻¹ (C-CH₃), and 1100 and 1043 cm⁻¹ (C-O). The NMR spectrum (CCl₄) had absorptions at δ 1.17 (s, 3H), 1.30 (s, 3H), 1.82 (m, 2H), 1.90 (m, 2H), 3.23 (s, 3H), and 4.83 (m, 1H). This spectral data is in agreement with that reported by Turro and Southam³ who isolated this compound from the photolysis of 2,2-dimethylcyclobutanone. A carbene intermediate was proposed by these authors and the same intermediate (CH_2) is probably involved in the photolysis of I.

The photolysis of the unsubstituted sulfur analog of I, thiacyclohexan-3-one with a 450W mercury lamp and a Pyrex 7740 filter, in 1,1,2-trichloro-1,2,2-trifluoroethane has been reported to also give a ring-contracted product (tetrahydrothiophen-2-one) and a ring-expanded

product (thiacycloheptan-4-one).⁴ The ring contracted product was not analogous to that found in our study. In *t*-butyl alcohol, thiacyclohexan-3-ol and *t*-butyl 5-thiahexanoate were isolated. No mechanism was proposed to explain these results. We believe that the photolysis of I involves two paths, one a cycloelimination followed by carbene formation and ring contraction, and the other, a hydrogen radical transfer to give II. These paths are indicated on Scheme I.



Initially I is excited to the $n\pi^*$ state (Ia). This is followed by a Norrish Type I cleavage to give an acyl-alkyl diradical (Ib). Intramolecular hydrogen abstraction in Ib can give the ketene (Ic) which then reacts with methanol to give II. This hydrogen radical transfer has been shown to occur for 2,2,5,5-tetramethyltetrahydrofuran-3-one through deuteration studies¹ and also in alicyclic ketones⁵. Alternatively the diradical Ic may undergo cycloelimination followed by carbene formation (Id). Acetone is formed in this step. 2-Propanol was produced by the photochemical reduction of this compound in methanol. The carbene intermediate is trapped by methanol to give III.

We are continuing the investigation of the photochemistry of isomeric tetrahydropyranones.

References:

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