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PHOTODIMERIZATION OF 2-BENZAL-4-PHENYLPSEUDOOXAZOLONE-5

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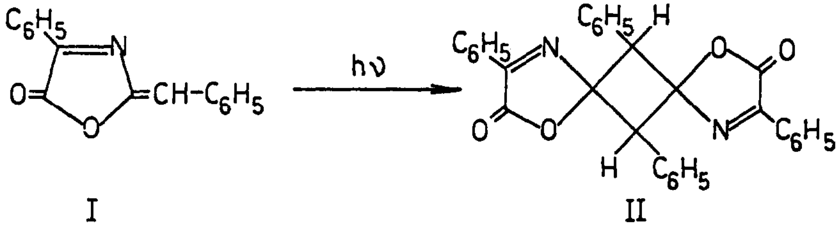
Few years ago one of us reported(1) the synthesis and the chemical behaviour of 2-benzal-4-phenylpseudooxazolone-5 (I). Recently it was noted that the U. V. spectrum of (I) decreases when exposed to the light(2). In order to study this behaviour we found it convenient to irradiate benzene solutions of (I), in glass vessels, with the light of a mercury lamp (Mazda 250 W). The irradiation produced a colourless compound (II), which gave (I) on heating near 240°C. The U. V. spectrum of (II), in cyclohexane, shows maxima at 208 nm ($\log\varepsilon = 4.40$), 218 nm ($\log\varepsilon = 4.43$), 298 nm ($\log\varepsilon = 4.42$), and shoulders near 228 nm ($\log\varepsilon = 4.12$) and 276 nm ($\log\varepsilon = 4.30$). In the I. R. spectrum of (II) a strong band at 1775 cm^{-1} is present as in that of (I). The above results together with the elemental analysis and the M. W. (493 osmometric in methyl ethyl ketone at 45°C) suggest that (II) is a dimer of (I) with the pseudooxazolonic portion unaltered.



I

II

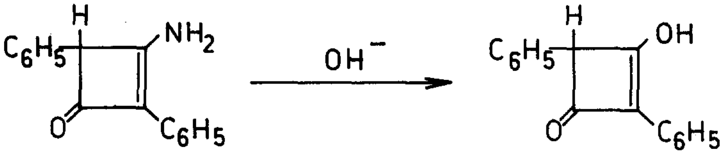
Filler and Piasek drew similar conclusions(3) for the product obtained by irradiating 2-benzal-4-methylpseudooxazolone-5 in the solid state.

An attempt to have additional data concerning the stereochemistry of (II) by recording the N. M. R. spectrum of (II) in $CDCl_3$ (TMS as internal standard), gave inconclusive results. In fact the signals obtained at δ 5.2 (s, 2, due to the CH of the cyclobutane ring), 7.22-7.5 (m, 16, protons of phenyl groups), and 8.2-8.4 ppm (m, 4, ortho protons of two phenyl groups) did not give sufficient evidence for a final statement on the stereochemistry of compound (II).

However the alkaline degradation of (II) shows that the photodimerization of (I) occurs with a head to tail mechanism on the exocyclic double bond. Thus compound (II) dissolved in THF was added with diluted NaOH (1.5%) at room temperature. After 15' THF was evaporated and a colourless product (III) (m.p. 170-172°C, from ethanol, M.W. 230 and the elemental analysis in agreement with the formula $C_{16}H_{13}NO$) was collected. The aqueous solution contained phenylglyoxylic acid also. The I.R. spectrum of compound (III) shows bands due to a $-NH_2$ (3340 and 3140 cm^{-1}) and to a -C=C-C=O system (1720 and 1640 cm^{-1}). The N.M.R. spectrum in DMSO-d_6 (TMS as internal standard) shows signals at δ 8.3, 7.68, 7.27, and 4.51 ppm (integral ratio 2:2:8:1) which were attributed respectively to a $-NH_2$ group (the signal disappears on deuteration), to two ortho protons of an aromatic system bonded to a highly polarized double bond, to eight aromatic protons, and to a -CH bonded to a phenyl ring. The U.V. spectrum, in methanol, shows two maxima (214 nm, log ε =4.30 and 268 nm, log ε =4.43) and a shoulder near 218 nm (log ε =4.28).

The above results can be explained when the effect of alkali solution on compound (I) is considered$^{(1)}$. Accordingly compound (II) reacted similarly to give 3-amino-2,4-diphenylcyclobuten-1-one (III) through the ring opening of the pseudooxazolonic portions.

The structure of compound (III) was confirmed by its conversion into 3-hydroxy-2,4-diphenylcyclobuten-1-one$^{(4)}$ on heating with alkali.



III

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