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PHOTOLYSIS OF 3-DIPHENYLHYDROXYMETHYL-4-DIPHENYLMETHYLENECYCLOBUT-2-EN-1-ONE

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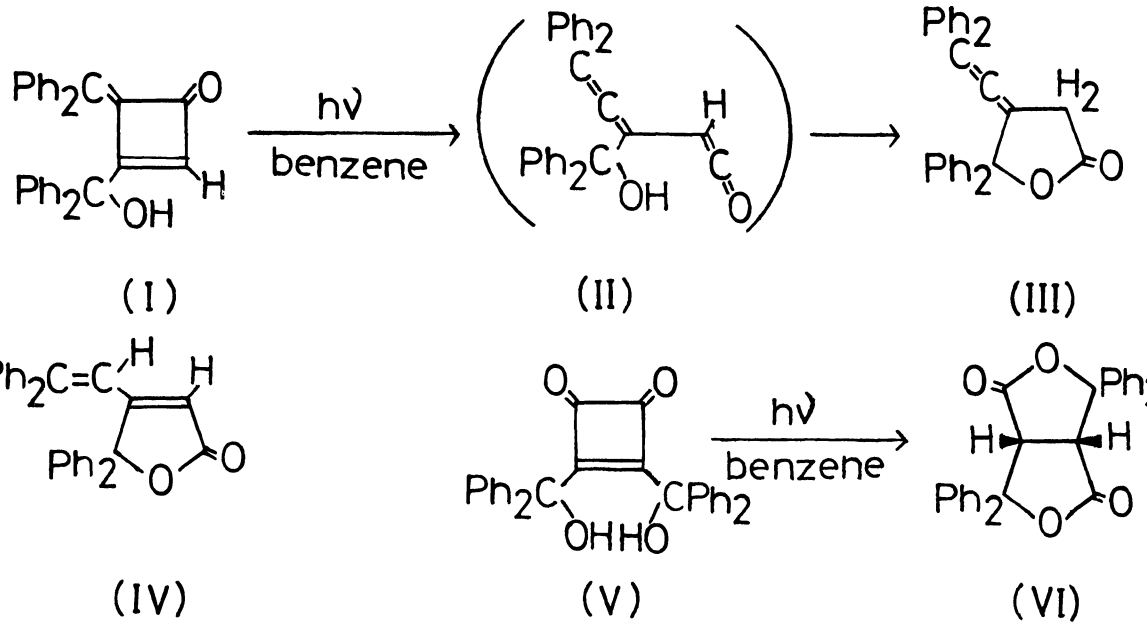
The photolysis of the title methylenecyclobutenone (I) in benzene afforded 5,5-diphenyl-4-diphenylvinylidene-1-oxacyclopentan-2-one (III) in 82% yield, probably via alleneketene intermediate (II). The photochemical conversion of 3,4-bis(diphenylhydroxymethyl)cyclobut-3-ene-1,2-dione (V) into 4,4,8,8-tetraphenyl-3,7-dioxabicyclo[3.3.0]octane-2,6-dione (VI) in 80% yield was also described.

The photochemical conversion of cyclobutenedione into bisketene intermediate via Norrish Type I reaction is well established.[1] In order to compare photolysis of methylenecyclobutenone with that of cyclobutenedione, we studied the photolysis of the title compound (I) in benzene and found that I affords 5,5-diphenyl-4-diphenylvinylidene-1-oxacyclopentan-2-one (III) probably via alleneketene intermediate (II) initially formed by Norrish Type I reaction of I.

Irradiation of a solution of I[2] (0.6 g) in benzene (150 ml) with a 100-W high-pressure mercury lamp under nitrogen at room temperature for 4 hr, afforded III (0.49 g, 82%), mp 112-113°C, as colorless needles. The structure of III was elucidated on the basis of the following spectral data: ir (nujol) 1790 (C=O), 1400 (CH_2), and 1205 cm^{-1} (lactone); uv $\lambda_{max}^{CHCl_3}$ 270 nm (ε, 14500); nmr $\tau_{CDCl_3}^{60MHz}$ 2.2-3.3 (m, Ph, 20H) and 6.35 (s, CH_2, 2H); mass m/e (rel intensity) 414 (M^+, 72), 386 (M^+-CO, 17), and 204 (386-Ph_2CO, 100). Although $\nu C=C=C$ of III was not observed in the ir spectrum, the presence of the allene linkage was proven by the detection of 1,1-diphenylbutatriene as the most intense fragment ion peak (m/e=204) in the mass spectrum.

A further structural evidence for III was obtained by the following reaction. Heating of III and KOH or K_2CO_3 in MeOH for 1 hr afforded the proton rearranged product, 4-(2,2-diphenylvinyl)-5,5-diphenyl-1-oxacyclopent-3-en-2-one (IV), mp 148-150°C, in 81% yield as pale yellow prisms. The structure of IV was elucidated on the basis of the following spectral data: ir (nujol) 1755 (C=O), 1625 and 1580 (C=C), 1220 and 1180 (lactone), and 970 cm^{-1} (=CH); uv $\lambda_{max}^{CHCl_3}$ 327 nm (ε, 19100); nmr $\tau_{CDCl_3}^{60MHz}$ 2.3-3.2 (m, Ph, 20H), 3.35 (s, =CH, 1H), and 4.85 (s, =CH, 1H); mass m/e (rel intensity) 414



(M^+, 7), 370 (M^+-CO_2, 84), 232 (M^+-Ph_2CO, 21), and 204 (232-CO, 100).

The formation of III can be rationalized in terms of the intramolecular esterification involving the alleneketene (II) as the intermediate which was produced by the α-cleavage of I similar to cyclobutenedione. Such an easy lactonization was demonstrated by photolysis of a hydroxymethylcyclobutenedione derivative. Thus, the photolysis of 3,4-bis(diphenylhydroxymethyl)cyclobut-3-ene-1,2-dione (V)[3] under the same conditions as those used for I resulted in a high yield (80%) of the 4,4,8,8-tetraphenyl-3,7-dioxabicyclo[3.3.0]octane-2,6-dione (VI), mp 227-228°C, colorless needles: ir (nujol) 1780 (C=O) and 1210 and 1180 cm^{-1} (lactone); nmr $\tau^{60MHz}_{CDCl_3}$ 2.6-3.2 (m, Ph, 20H) and 5.85 (s, CH, 2H); mass m/e (rel intensity) 446 (M^+, 100), 402 (M^+-CO_2, 7), 358 (M^+-2CO_2, 15), 264 (M^+-Ph_2CO, 70), and 236 (264-CO, 62).

References

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