Divergence of the Photochemical Reaction of Cyclo-octa-2,6-dienone

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Summary The course of the photochemical reaction of cyclo-octa-2,6-dienone is affected by wavelength of light, reaction temperature, and added cuprous salt.

THE photolysis of *cis,cis*-cyclo-octa-2,6-dienone (**1**) was recently reported to involve both rearrangement to 6-vinylcyclohex-2-enone (**2**) and isomerisation to *trans,cis*-cyclo-octa-2,6-dienone (**8**).[1] The conjugated enone (**2**) was further transformed photochemically to tricyclo[3,3,0,$0^{2,7}$]-octan-6-one (**3**), while the sterically constrained *cis,trans*-dienone (**8**) was thermally trapped with methanol and furan to form the polar adduct (**9**)[2] and the cycloadduct (**10**), respectively. We report our findings on the same subject, including the influences of wavelength of incident light, reaction temperature, and cuprous salt.[3]

The u.v. spectrum of (**1**) (MeOH) shows absorption maxima at 227 (log ϵ 3·86) and 320 nm (1·99).[1] Irradiation† of a 0·2% methanol solution of (**1**) with light of wavelength >350 nm (aq. $CuSO_4$ as filter) for 30 min gave (**9**) as the sole product in 85% yield. By contrast, exposure to unfiltered light for 6 min resulted in formation of a complex mixture consisting mainly of (**2**) (5%), (**3**) (2%), (**9**) (78%), and unreported products, methyl 3-cyclohexenylacetate (**6**) (2%) and methyl 2-vinylcyclobutylacetate (**7**) (6%, 2

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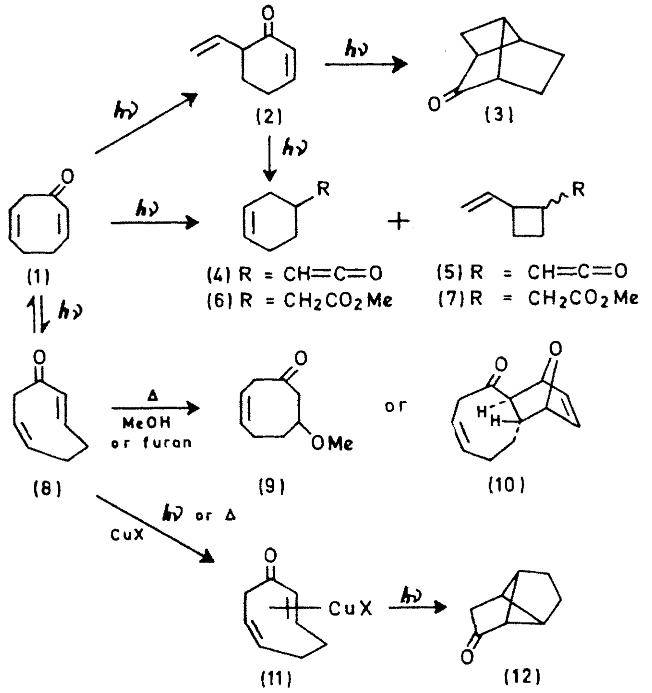
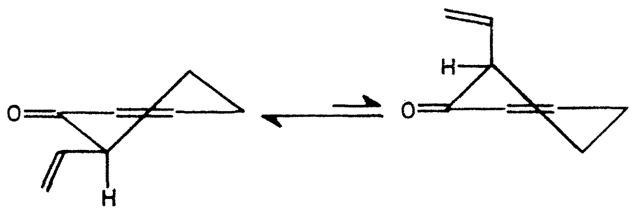
† Unless otherwise stated, photolysis was conducted externally using a 200 w high-pressure mercury arc at room temperature under a nitrogen atmosphere.

isomers).‡ Products derived from photolysis of (**9**)[4] were also obtained in varying yields. Precursors of the methyl esters (**6**) and (**7**) would most probably be the ketens (**4**) and (**5**) which could be produced photochemically from the dienones (**1**), (**2**), and (**8**). In fact, an i.r. spectrum (at −150°) of (**1**) (neat) which had been photolysed through NaCl windows exhibited a sharp absorption at 2105 cm^{-1} characteristic of the keten group.



The observed wavelength-dependence of the course of the reaction would imply that the rearranged products (**2**), (**4**), and (**5**) arise from the π,π^* singlet states of the dienones or the n,π^* triplet states formed therefrom, whereas the π,π^* triplet states of (**1**) and (**8**) induce the *cis–trans*-isomerisation of the conjugated double bond. The reported effects of triplet sensitizers and quenchers are also in accord with this speculation.[1]

Photolysis of a 0·2% ethereal solution of (**1**) at −78° (methanol–Dry Ice bath) for 1 h, followed by addition of methanol, afforded (**2**) (15%) besides (**6**), (**7**), and (**9**) (8, 8, and 40%, respectively), but *did not* give the tricyclic ketone (**3**).§ This is in contrast with the previous claim that irradiation of (**1**) at 10° affords (**3**) in modest yield.[1] This temperature effect could readily be explained if the enone (**2**) is assumed to exist in the equilibrating conformations (**2a**) ⇌ (**2b**). Models suggest that the internal cycloaddition forming (**3**) is attainable only with the latter conformation in which the vinyl group is situated in the quasi-axial position, though the geometry in the excited state would be distorted to some extent from that of the ground-state molecule. Hence the absence of (**3**) in the photolysate obtained at −78° could be ascribed to the decreased population of the less stable conformer (**2b**) at low temperature.¶



(2a) (2b)

Finally, the photolysis of (**1**) in the presence of cuprous salt proceeds quite differently. When a mixture of (**1**) (12 mmol.) and cuprous chloride (50 mmol.) in tetrahydrofuran (300 ml) was exposed to unfiltered light, tricyclo$[3,3,0,0^{2,6}]$octan-3-one (**12**) was obtained as the major product (25—30%). The structure was confirmed by comparison of the spectral data with literature values.[6] The 2,4-dinitrophenylhydrazone had m.p. 205—206° (lit.,[6] 206—207°). The present transformation is reminiscent of the well known cuprous chloride-catalysed photoisomerisation of cyclo-octa-1,5-diene to tricyclo$[3,3,0,0^{2,6}]$octane.[7] The fact that the formation of (**12**) was chemically quenched by furan would suggest that the cyclo-conversion proceeds by way of the *cis,trans*-dienone–copper complex (**11**). The possibility that the tricyclic ketone (**12**) might be produced by a thermal reaction of the highly reactive dienone (**8**) under the influence of the copper salt was excluded by control experiments: when a tetrahydrofuran solution containing (**1**) and (**8**) was mixed with a large excess of cuprous chloride and kept at room temperature for extended periods, no trace of (**12**) was obtained.

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‡ All new compounds gave correct elemental analyses and/or molecular peaks in mass spectra. The assigned structures were also supported by u.v., i.r., and n.m.r. spectra.

§ It was reported[1] that photolysis at −70° gave (3) in low yield, no trace of (2) being detected. However, we could not reproduce this result.

¶ Short-wavelength light (low-pressure mercury arc) is only slightly effective in the transformation of (2) to (3). This is consistent with the previous observation in the related photoisomerisation of isopiperitenone (ref. 5).

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