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THE STEREOCHEMICAL FATE OF THE DIRADICAL INTERMEDIATE IN THE PHOTOLYSIS OF CYCLODODECEN-2-ONE

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cis-Cyclododecen-3-one (III) was reported[3] to be the only photoproduct of *trans*-cyclododecen-2-one (I). This result implies that: i) the diradical intermediate (V) formed by γ-hydrogen abstraction of *cis*-cyclododecen-2-one (II) evolves stereoselectively to the *trans*, *cis*-cyclododeca-1,3-dienol (VI), which in turn tautomerizes to (III); ii) the *cis*-cyclododecene-3-one (III) is unusually stable to u.v. irradiation. However, α,β-unsaturated ketones are known[4] to suffer u.v. promoted γ-hydrogen abstraction to give mixtures of the isomeric *cis* and *trans* β,γ-unsaturated ketones; in these compounds[5] and in their γ,δ-analogues[6] the *cis*-*trans* interconversion occurs readily.

In the effort to reconcile Nozaki's unprecedented result[3] with the above cited reports, we investigated more closely the photochemical behaviour of the *trans*-cyclododecen-2-one.

trans-Cyclododecen-2-one [(I), 5% in cyclohexane, 50 ml] was irradiated (internally, Pyrex apparatus thermostatted at 20° C) with a 125 watt high pressure Hg lamp: after 8 hr both the *cis*- and the *trans*-cyclododecen-3-one (III) and (IV) were formed (yield >90%*) in a 84:16 ratio, by v.p.c.** (all glass analytical apparatus: silanized column, 2 m, 3% NPGS on

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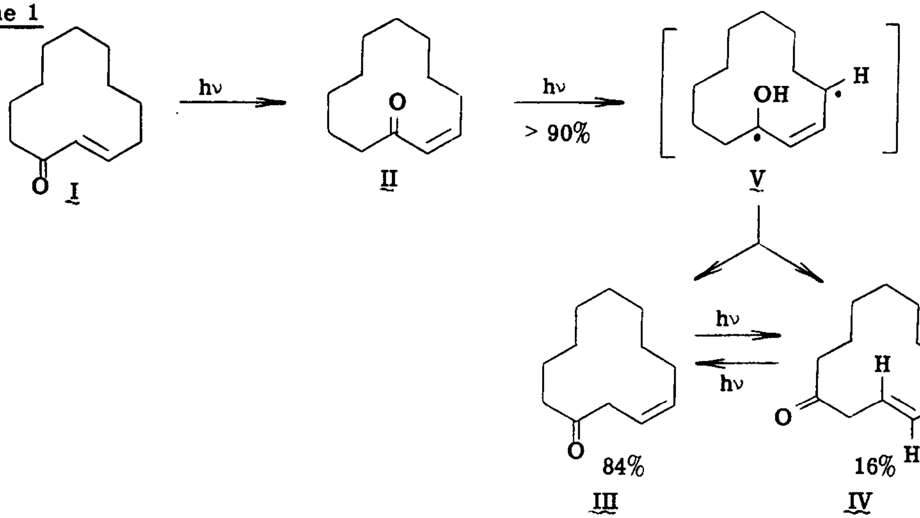
*A high melting material, presumably a dimer, was also obtained in ~1% yield.

**The analytical v.p.c. conditions under which the crude reaction mixture was reported[3] to give a single peak were inadequate to detect successfully the *trans*-isomer: in fact the properties reported for the ketone (III) are consistent with a mixture of (III) and (IV).

silanized Chromosorb W, 80-100 mesh, 150°). Four fractional crystallizations from n. pentane afforded the cis-isomer in a pure state [(III), m.p. 50, lit.[3] 39; I.R. (nujol): $\nu_{C=O}$ 1698 cm^{-1}; $\lambda_{max}^{EtOH\ 95\%}$ 289 (log ϵ = 1.77); ^{1}Hnmr* (CDCl$_3$): 4.26 τ, dtt H_β, 4.58 τ, dtt H_ν, 6.80 τ, dd H_α, 7.59 m, $H_{\alpha'}$, 7.85 τ m -CH$_2$-C=, 8-9 τ (10H) CH$_2$: $^3J_{\beta\gamma}$ 11, $^3J_{\alpha\beta} = {}^3J_{\nu\delta} = 7.5$, $^4J_{\beta\delta} = {}^4J_{\alpha\nu} = 1.25$]. Fractional crystallization of the residue from mother liquors of (III) afforded in low yield the trans-cyclododecen-3-one [(IV), m.p. 28-29; I.R. (film) $\nu_{C=O}$ 1705 cm^{-1}, $\nu_{C=C}$ 1660 cm^{-1}, $\nu(\overset{H}{\ }\!\!\diagdown C{=}C\diagdown_{H})$ 978 cm^{-1}; $\lambda_{max}^{EtOH\ 95\%}$ 294 (log ϵ = 2.75); ^{1}H nmr (CDCl$_3$): 4.36 τ dtt H_β, 4.62 τ dtt H_γ, 6.98 τ dd H_α, 7.54 τ m $H_{\alpha'}$, 7.94 τ m -CH$_2$-C=, 8-9 m (10H) CH$_2$; $^3J_{\beta\gamma} = 15.2$, $^3J_{\alpha\beta} = {}^3J_{\gamma\delta} = 7$, $^4J_{\beta\delta} = {}^4J_{\alpha\gamma} = 0.7$ Hz].

Scheme 1



The observation that the cis-β,γ-unsaturated ketone (III) isomerized (~80%) into the trans-β,γ-ketone (IV) when injected in a v.p.c. apparatus working on preparative conditions enabled us to obtain substantial amounts of mixtures rich in (IV): from these mixtures trans-cyclododecen-3-one (IV) could be obtained in moderate yield by several fractional crystallizations.

trans-Cyclododecen-3-one (IV) underwent conversion into cis-cyclododecen-3-one (III) upon irradiation (1% cyclohexane, 50 ml) in the same apparatus as before. After 6 hr a photostationary mixture of (III) to (IV) in the ratio 84:16 was obtained (Fig. 1). Irradiation of pure (III) led to the same steady state mixture.

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*At 100 MHz, first order analysis

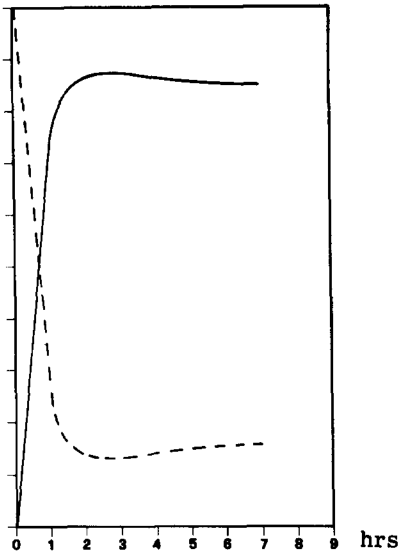


Figure 1

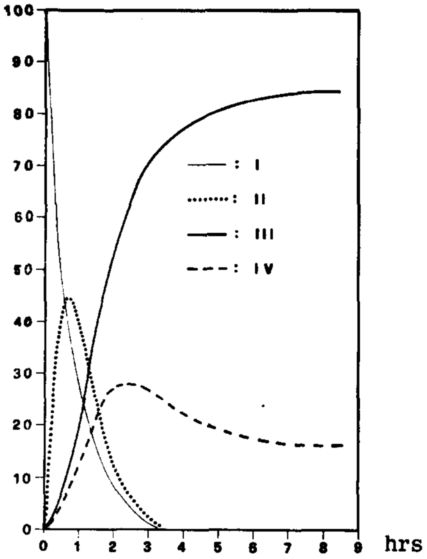
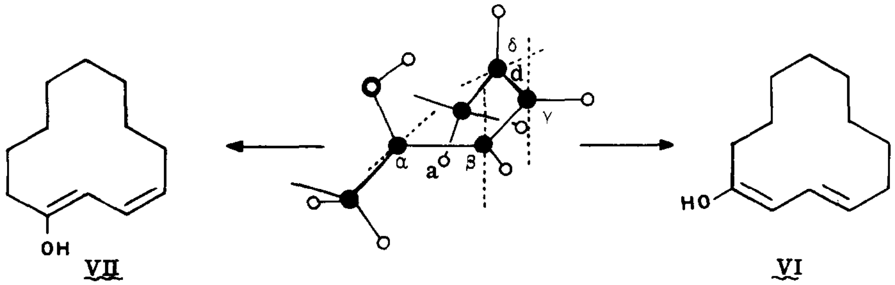


Figure 2

The progress of the photochemical isomerization I ⟶ III + IV was monitored by periodic withdrawal of aliquots and examining them by analytical v.p.c. (Fig. 2), without elimination of the solvent. At low conversions the concentration of cis-cyclododecen-2-one (II)[3] increases to a maximum value of 45% (45 min): this product undergoes rapid conversion into a mixture of (III) and (IV) which is richer in (IV) (30% after 2 hrs) than the photostationary state mixture (16% after 8 hrs).

The foregoing results prove that: i) both the cis- and trans-cyclododecen-3-ones (III) and (IV) are not photochemically stable but are capable of interconversion to reach a photostationary state. This is sound on considering that intramolecular energy transfers in β,γ-unsaturated carbonyl compounds are a common process; ii) the trans-cyclododecen-3-one (III) is formed directly from the cis-cyclododecen-2-one (II) via the diradical intermediate (V):

Scheme 2



iii) the bis allylic diradical (V) is an intermediate common both to (III) and to (IV); iv) the stereochemical fate of the diradical intermediate (V) is not greatly influenced by the conformational preferences[7] of the medium ring. In the diradical (V) free rotation is expected both at the a and the d bond. Accordingly the dienol (VI) arises (Scheme 2) by counterclockwise rotation of the C_γ carbon p orbital while the dienol (VII) arises through a clockwise rotation of the C_γ carbon p orbital associated with the clockwise 180° rotation of the C_α carbon p orbital: judging from models the two rotations are probably simultaneous since the *trans*,*trans*-cyclododeca-1,3-dienol has very little chance for formation.

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