The Photolysis and Pyrolysis of Cyclo-oct-4-enone

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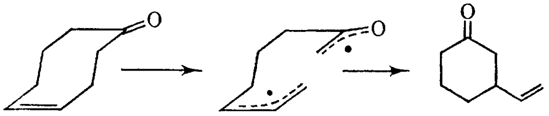
IN connection with studies on the interaction of formally nonconjugated chromophores in photochemical transformations, we have examined the photolysis of cyclo-oct-4-enone (I) and find that the major reaction involves a unique conversion into 3-vinylcyclohexanone (II). Thus, irradiation of a 1% solution of (I) [$\lambda_{\max}$ (hexane) 289 mμ, ϵ 13] in cyclohexane (450 w Hanovia source, Vycor filter) until about half of the starting material was consumed, gave a 62% recovery of distilled product which consisted of 35% recovered (I) and 34% (II) with a dozen minor components constituting the remainder. The structure of (II) rests on its physical properties [satisfactory analysis; infrared: 5·82, 6·1, 10·1, and 10·9 μ; n.m.r.: τ 4·2 (1H, m), 5·0 (2H, m), and 7·3—8·6 (9H); mass spectrum: important peaks at *m/e* 124, 96, 81 (base), 67, 55, and 54] and comparison with a sample obtained by the hydration[1] of 4-vinylcyclohexene and subsequent chromic acid oxidation. Compound (II) undergoes further reaction but does not revert to (I) photochemically.


(I) (III) (II)

Several acyclic $\gamma\delta$-unsaturated ketones have been subjected to photolysis.[2] The major characterized reactions of such molecules are intramolecular oxetan formation and *cis–trans*-isomerization of the olefinic moiety. The latter process is thought to involve intramolecular energy transfer and this phenomenon has been suggested to account for the special stability of $\gamma\beta$-unsaturated ketones toward Norrish type I bond cleavage. In the present instance type I cleavage is secondary to the process leading to (II). We suggest that this latter conversion proceeds *via* diradical (III), a species derived by homolysis of the C–C bond β to the carbonyl group. Such a process is unprecedented in solution photochemistry, although similarly disposed C–Cl bonds suffer an analogous cleavage.[3] The importance of this reaction in the cyclic system provided by (I) is attributed to the high population of conformations, such as the one illustrated, in which there can be essentially full overlap of the incipient radical centres with the neighbouring π-systems in the transition state for homolysis. Energy transfer from the carbonyl group to the olefin moiety, with or without isomerization to the strained *trans*-isomer of (I), may precede actual bond breakage, but the stereoelectronic situation will be much the same.

Flow pyrolysis of (I) at 720° also converts (I) into (II) efficiently (41% isolated yield). The rest of the product consists of starting material (9%), octa-1,7-dien-3-one (7%), and a plethora of minor constituents (9%). Compound (II) is stable to the reaction conditions in this case. Further elaboration of the details of these interesting alternate high-energy transformations of (I) and their possible relationship is the object of our further work.

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