Cyclohexa-2,4-dienone–Dienketen Valence Isomerisations: Thermal and Photochemical Interconversions

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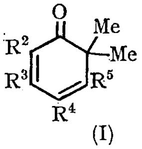
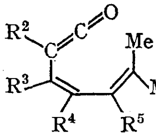
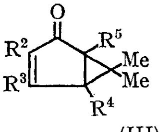
RECENT investigations of the photochemistry of cyclohexa-2,4-dienones (I) have revealed some curious features.[1] Irradiation of compounds bearing few substituents results in the usual Barton–Quinkert type of ring cleavage[2] to give transient dienketens (II), which are converted into 3,5-dienoic acid derivatives in protic media.[2,3] Certain more highly substituted compounds however, particularly those bearing a 2-alkyl group, are either inert to irradiation in ether or methanol, or are isomerised to bicyclo[3,1,0]hexenones (III). In these cases, on the assumption that reaction of a keten such as (II) with protic solvents would be very rapid, it has been concluded by Collins and Hart that ring cleavage does not occur, and that the dienketens are unlikely to be precursors of the bicyclic compounds.[1]



(I)



(II)

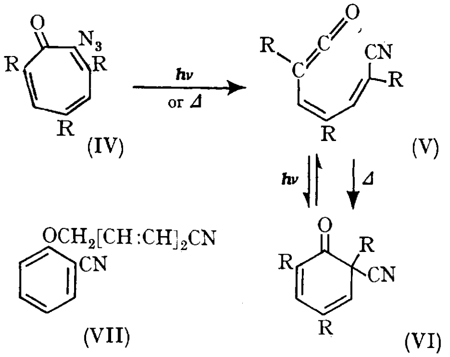


(III)

The availability of dienketens having the same geometry from thermolysis or photolysis of 2-azidotropones (IV)[4] provides an opportunity to study their properties independently of cyclohexadienone precursors, and we report here data concerning the two ketens (Va) and (Vb).

Photolysis† of hexane solutions of the azides (IV) resulted in rapid and complete replacement of their characteristic 325—400 mμ absorption by intense peaks (see Table) ascribed to the dienketens (V). Only the unsubsituted compound (Va) was sufficiently long-lived ($t_{\frac{1}{2}}$ at 22°, 4 min.) to be observable at room temperature. Its relatively slow conversion, *via* (VIa) into a mixture consisting mainly of the ester (VII), plus traces of *o*-salicylonitrile,[4] permitted observation of keten i.r. absorption at 2120 cm.$^{-1}$ as an intense peak, immediately quenched by addition of methanol.

The thermal decay of this intermediate, readily followed by monitoring its absorbance at 313 mμ, showed eventual deviation from first-order kinetics, presumably due to intrusion of the second-order process responsible for the formation of (VII); the rate constant quoted must therefore be regarded as an upper limit.



a, R=H; b, R=Me

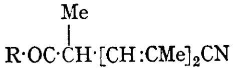
A comparable half-life was attained by the trimethyl compound (Vb) only at −50°; at ambient temperatures, rapid and quantitative conversion of the azide (IVb) into the dienone (IVb), λ_{max} 308 mμ (ε 4000) was evident from the well-defined isosbestic points in repetitive scans of the u.v. spectrum of a solution undergoing photolysis. At lower temperatures, the formation of (Vb), and its clean first-order conversion into (VIb) were readily monitored by u.v. spectroscopy. The rate data (see Table) lead to reaction parameters $\Delta H^{\ddagger} = 13{\cdot}9$ kcal./mole and $\Delta S^{\ddagger} = -3{\cdot}5$ e.u., reflecting the remarkable facility of this cyclisation compared with other acyclic hexatriene–cyclohexadiene valence isomerisations.[5] Extrapolation to 22° leads to a cyclisation rate for the trimethyl-keten (Vb) of *ca.* 10^3 times that of the unsubstituted compound (Va), evidently sufficiently fast to compete with attack by nucleophilic solvents. Thus, while thermolysis of the azide (IVa) in aqueous dioxan or methanol gave only products derived from solvent addition to the keten (Va),[4] the trimethyl analogue (IVb) gave, in addition to (VIII), 50 and 25% respectively of the dienone (VIb) under the same conditions. Only in cyclohexylamine was all material recovered as acyclic product (VIII; R = $C_6H_{11}NH$).

TABLE

Keten	λ_{max}mμ (ε)[a]	Temp.	10^5k (sec.$^{-1}$)
(Va)	313 (15,500)[b] 323sh (12,500)	22°	290
(Vb)	324 (11,500)	−77°	2·2
	221 (14,000)	−50°	190

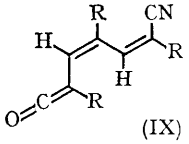
[a] Maximum observed intensity. [b] Correction for material present as product (VII), estimated from absorbance at 251 mμ, leads to a value for ε in the region 25,000—30,000.

The rate-enhancing effect of alkyl substituents on the dienketen cyclisation[2] presumably results from beneficial steric influences, *e.g.*, the undesirable s-*trans*-arrangement (IX) should be less favoured where R = Me than with R = H. Hence, promotion of thermal, and probably also photochemical,[2] recyclisation, relative to solvent addition, may account for the failure to trap ketens generated from highly substituted dienones at ordinary temperatures.



$$\mathrm{R{\cdot}OC{\cdot}\overset{\overset{\displaystyle Me}{|}}{C}H{\cdot}[CH{:}CMe]_2CN}$$

(VIII)



(IX)

Irradiation (Pyrex filter) of the dienone (VIb) at −77° resulted in rapid regeneration of the dienketen spectrum; the maximum absorbance attained at 324 mμ corresponded to 57% of that initially developed in the azide photolysis. Further irradiation resulted in gradual diminution of this peak, with eventual loss of all well-defined absorp-

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† Solutions (*ca.* 10^{-4}M) were photolysed in the sample compartment of a Cary model 14 spectrophotometer, using the tungsten near-infrared source fitted to this instrument in conjunction with a plate-glass filter.

tion > 230 mμ. This result differs strikingly from that of photolysis at room temperatrue, at which the stationary concentration of dienketen must be very small. In this case a new peak at 257 mμ appeared, associated with a product, as yet unidentified, having an i.r. band at 1708 cm.$^{-1}$. Further studies are required to explore the implication that the dienone (VIb), and its associated dienketen (Vb), give rise to different photoproducts.

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[2] D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1960, 1; G. Quinkert, *Angew. Chem. Internat. Edn.*, 1965, **4**, 211.

[3] P. M. Collins and H. Hart, *J. Chem. Soc.* (*C*), 1967, 1197.

[4] J. D. Hobson and J. R. Malpass, *Chem. Comm.*, 1965, 141; *J. Chem. Soc.* (*C*), 1967, 1645.

[5] *e.g.*, E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Letters*, 1965, 385; E. Vogel, W. Grimme, and E. Dinne, *ibid.*, p. 391.