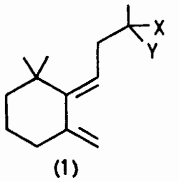
Photochemistry of Dienones. Part 6.[1] On the Reacting Excited States of Retro-γ-Ionones

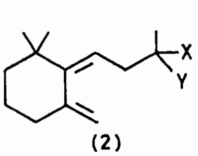
By **Hans Cerfontain** * and **Jan A. J. Geenevasen**, Laboratory for Organic Chemistry, The University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

(*E*)- and (*Z*)-retro-γ-ionone (1a) and (2a) and (*E*)-retro-γ-ionol (1b) upon triplet photosensitization undergo only (*Z*)–(*E*) isomerization. The bicyclo-octene derivatives (3a and b) and the tricyclic oxetan (4) obtained upon direct irradiation of, respectively, (1a), (1b), and (2a) at λ 254 nm result from the excited singlet states. From the dependence of the photostationary state ratio on the triplet energy of the sensitizer it was concluded that the triplet energies of (*Z*)- and (*E*)-retro-γ-ionone and (*Z*)- and (*E*)-retro-α-ionone are 73 ± 2, 60 ± 2, 65 ± 1, and 60 ± 2 kcal mol^{-1} respectively.

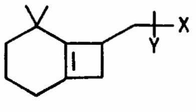
SOME time ago we reported on the photochemistry of some ionone compounds.[1,2] We showed that upon irradiation at 254 nm (*E*)-retro-γ-ionone (1a) and (*E*)-retro-γ-ionol (1b) yield the bicyclic isomers (3a and b) respectively, whereas (*Z*)-retro-γ-ionone (2a) yields the tricyclic oxetan (4). The present study was set up to determine amongst others the multiplicity of the reacting excited states of (*E*)- and (*Z*)-retro-γ-ionone.



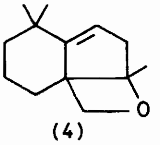
(1)
a; X,Y=O
b; X=H,Y=OH



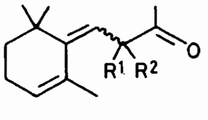
(2)



(3)



(4)

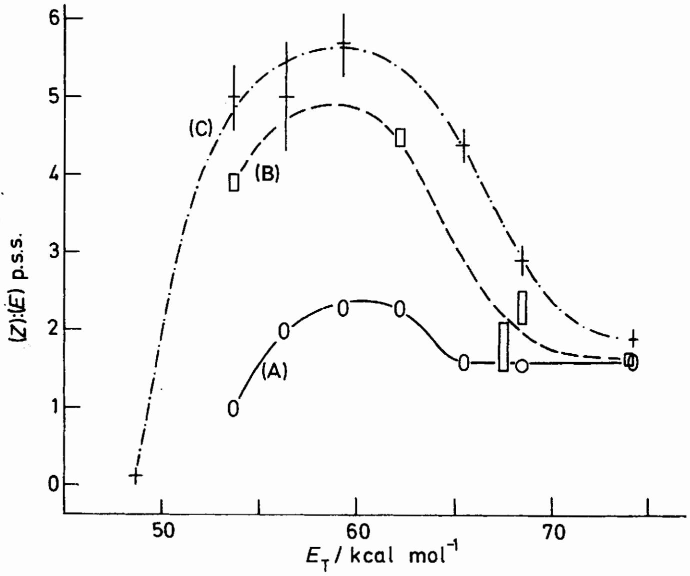


(5)
a; R^1=H, R^2=Me
b; R^1=R^2=Me

RESULTS AND DISCUSSION

The products of (*E*)-retro-γ-ionone (1a) and the corresponding ionol (1b) upon direct irradiation in benzene are the bicyclic octene derivatives (3a and b) respectively. Under similar conditions (*Z*)-retro-γ-ionone (2a) yields the tricyclic oxetan (4) (Table 1). Upon triplet photosensitization only (*Z*)–(*E*)-isomerization is observed. Accordingly, it is concluded that the intramolecular [2 + 2] cycloadditions of (*E*)- and (*Z*)-retro-γ-ionone and (*E*)-retro-γ-ionol are excited singlet state reactions. Only the (*E*)-isomers (1a and b) yield exclusively the cyclobutenes, because of release of steric strain between the alkylidene side chain and the dimethylene moiety of the six-membered ring. By contrast, the allylic hydrogens of the side chain of the (*Z*)-isomers (2) prohibit cyclobutene formation because of repulsive steric interaction with the exocyclic methylidene group. With (*Z*)-retro-γ-ionone this interaction in fact places the carbonyl and the exocyclic methylidene groups in a mutually favourable position to undergo intramolecular [$2\pi_{CO} + 2\pi_{CC}$]cycloaddition with formation of (4).

As regards the geometric isomerization, the photostationary (p.s.s.) (*Z*) : (*E*) ratio obtained in the benzophenone photosensitized isomerization is substantially greater for retro-γ-ionol than for retro-γ-ionone (Table 1). This may be explained in terms of a difference in steric hindrance of the geometric isomers involved. A careful study of molecular models did show that steric interactions relevant to the (*Z*)–(*E*)-isomerization are the same for (*Z*)-retro-γ-ionol and (*Z*)-retro-γ-ionone, whereas there is a greater repulsive steric interaction in the (*E*)-retro-γ-ionol than in the corresponding ionone. The



Photostationary states obtained in the photosensitized isomerization of the two retro-α-ionones (A) and (B) (□) and retro-γ-ionone (1a) (C) as a function of the triplet energy of the sensitizer

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[1] Part 5, A. van Wageningen, H. Cerfontain, and J. A. J. Geenevasen, *J.C.S. Perkin II*, 1975, 1283.

[2] (*a*) A. A. M. Roof, A. van Wageningen, C. Kruk, and H. Cerfontain, *Tetrahedron Letters*, 1972, 367; (*b*) A. van Wageningen and H. Cerfontain, *Tetrahedron Letters*, 1972, 3679; (*c*) A. van Wageningen, P. C. M. van Noort, and H. Cerfontain, *J.C.S. Perkin II*, 1974, 1662.

dependence of the photostationary (*Z*) : (*E*) ratio of the retro-γ-ionones on the triplet energy of the photosensitizer (Figure) is similar to those of *e.g.* retro-α-ionones (5) [2c] and the piperylenes [3] in that a constant (*Z*) : (*E*) ratio is approached at high triplet energy values and that there is a maximum at lower E_T values. The high energy limiting (*Z*) : (*E*) ratios are about the same for the three sets of geometric isomers studied. Based

$$^3S + (Z)\text{-D} \longrightarrow S + {}^3[(Z)\text{-D}] \qquad (1a)$$

$$^3S + (E)\text{-D} \longrightarrow S + {}^3[(E)\text{-D}] \qquad (1b)$$

$$^3[(Z)\text{-D}] \longrightarrow \text{D}(T) \qquad (2a)$$

$$^3[(E)\text{-D}] \longrightarrow \text{D}(T) \qquad (2b)$$

$$\text{D}(T) \longrightarrow (Z)\text{-D} \qquad (3a)$$

$$\text{D}(T) \longrightarrow (E)\text{-D} \qquad (3b)$$

$$^3S + (Z)\text{-D} \longrightarrow S + \text{D}(T) \qquad (4a)$$

$$^3S + (E)\text{-D} \longrightarrow S + \text{D}(T) \qquad (4b)$$

on careful mechanistic studies on the isomerizations of a (di)ene (D) induced by triplet excited sensitizer (^3S),[3,4] it was concluded by Wagner and Hammond [5] that in the high energy region triplet energy transfer occurs to both isomers at a diffusion controlled rate [by (1a and b)], and that the observed (*Z*) : (*E*) p.s.s. ratio is the actual decay ratio of the common (twisted) intermediate D(*T*), k_{3a}/k_{3b}. The higher (*Z*) : (*E*) ratios at lower triplet energy represent slower nonvertical transfer to the (*Z*)-isomer [step (4a)], while transfer to the (*E*)-isomer [*via* (1b)] retains maximum efficiency (*cf.* ref. 6). At still lower triplet energy also the vertical transfer to the (*E*)-isomer becomes endothermic and slower nonvertical transfer occurs by (4b). From these considerations and the data in Table 1 and the Figure the triplet energies of (*Z*)- and (*E*)-retro-γ-ionone and the (*Z*)- and (*E*)-retro-α-ionone were estimated. The results are collected in Table 2, together with those of the piperylenes for comparison. It is noteworthy that the triplet energies of (2a) and (*Z*)-retro-α-ionone are significantly higher than those of the piperylenes. The high value of (2a) may be related to the non-coplanarity of its diene system.* The spuriously high photostationary (*Z*) : (*E*)

TABLE 1

Excited state reactions of (*E*)- and (*Z*)-retro-γ-ionones and the corresponding ionols in C_6H_6

Substrate	Sensitizer	E_T/kcal mol^{-1} [a]	λ/nm	Products, other than resulting from (*E*)–(*Z*) isomerization	Irradiation time (ks) required to obtain a (*Z*) : (*E*) ratio of 1	Photostationary state [(*Z*) : (*E*)]
(1a)			300 [b]	Bicyclic ketone		
(1a)	Pyrene	48.7	366 [c]			0.12 ± 0.01
(1a)	Benzil	53.7; 50.9 [d]	366 [c]		20.0	5.0 ± 0.4
(1a)	1-Acetonaphthone	56.4	366 [c]		17.0	5.0 ± 0.7
(1a)	2-Acetonaphthone	59.3	366 [c]		14.8	5.7 ± 0.4
(1a)	Phenanthrene	62.2	366 [c]		34.4	13.3 ± 2.0
(1a)	Thioxanthone	65.5	366 [c]		4.7	4.4 ± 0.2
(1a)	Fluorene	67.6	366 [c]		25.6	24 ± 4
(1a)	Benzophenone	68.5	366 [c]		9.0	2.9 ± 0.2
(1a)	Xanthone	74.2	366 [c]		8.5	1.9 ± 0.1
(2a)			300	Tricyclic oxetan		
(2a)	Benzophenone	68.5	366 [c]			3.0 ± 0.2
(1b)			254	Bicyclic alkanol		
(1b)	Benzophenone	68.5	366 [c]			9.0 ± 1.5
(2b)	Benzophenone	68.5	366 [c]			9.0 ± 1.5

[a] Ref. 9, p. 92. [b] In the absence of irradiation almost no bicyclic ketone is formed. [c] More than 99% of the radiation is absorbed by the sensitizer. [d] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 1960, **14**, 48; J. C. Dalton, B.Sc. Thesis, California, Institute of Technology, 1964 (*cf.* W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, 1966, **88**, 4769).

TABLE 2

Triplet energies of some ionones and the piperylenes

Compound	Configuration of the photoisomerable double bond	Configuration of the diene C(2)–C(3) bond	E_T/kcal mol^{-1}
(1a)	*E*	single-*Z*	60 ± 2
(2a)	*Z*	single-*Z*	73 ± 2
(*E*)-(5a)	*E*	single-*E*	60 ± 2
(*Z*)-(5a)	*Z*	single-*E*	65 ± 1
(*E*)-C_5H_8	*E*	single-*E*	58.8 [a]
(*Z*)-C_5H_8	*Z*	single-*E*	56.9 [a]

[a] From R. E. Kellog, cited in ref. 3.

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* The non-coplanarity of the diene system of (2a) may be concluded from the observation that $\lambda_{max.}$ of the π–π^* absorption of (2a) is substantially smaller (208 nm) than the one calculated on the basis of the Woodward rules,[7a] *i.e.* for the planar configuration (*ca.* 240 nm). For the basic 1,2-dimethylenecyclohexane system $\lambda_{max.} = 220$ nm.[7b]

[3] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

[4] (*a*) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, 1966, **88**, 4769; (*b*) L. M. Coyne, *Diss. Abs.*, 1967, **28**, 515–B; (*c*) R. S. H. Liu and D. M. Gale, *J. Amer. Chem. Soc.*, 1968, **90**, 1897; (*d*) R. A. Caldwell and R. P. Gajenski, *ibid.*, 1971, **93**, 532; (*e*) R. A. Caldwell, G. W. Sovocool, and R. J. Peresie, *ibid.*, 1973, **95**, 1496.

[5] P. J. Wagner and G. S. Hammond, in 'Advances in Photochemistry,' eds. W. A. Noyes, jun., G. S. Hammond, and J. N. Pitts, jun., Wiley, New York, 1968, vol. 5, pp. 72*ff*.

[6] S. Yamanchi and T. Azumi, *J. Amer. Chem. Soc.*, 1973, **95**, 2709.

[7] H. H. Jaffé and M. Orchin, 'Theory and Application of Ultraviolet Spectroscopy,' Wiley, New York, 1962, (*a*) pp. 218—219; (*b*) pp. 201—203.

ratios observed for phenanthrene and fluorene indicate that for these addenda additional routes for sensitization are operative.[8] Two such routes may be considered, *viz.* (i) *via* singlet energy transfer,[9] and (ii) *via* exciplex formation.[10] The first explanation can be ruled out as singlet excited (*E*)- and (*Z*)-retro-γ-ionone would yield the bicyclo-octene (3a) and the tricyclic oxetan (4) respectively (see earlier). In fact, in the phenanthrene and fluorene photosensitized reaction of both (*E*)- and (*Z*)-retro-γ-ionone compounds (3a) and (4b) are not formed beyond the limits of detection which is 2% of the total amount of isomers. This leaves the second explanation, *i.e.* a route *via* exciplex formation. Evidence for exciplex formation between substrate and sensitizer was very recently obtained for the fluoren-9-one photosensitized isomerization of the α-pyran (5).[11]

EXPERIMENTAL

The retro-γ-ionones and the corresponding ionols were prepared as described.[12] (*E*)-Retro-γ-ionone was also obtained by direct irradiation of (*E*)-β-ionone (0.1 mol) in ethanol with λ 254 nm (Rayonet RPR-208) for 16 h and subsequent removal of the solvent and preparative g.l.c. on a copper column (5 m, diam. 9 mm, 15% SE-30 on Chromosorb W 45—60 mesh, 120°, 80 ml He min^{-1}). The photosensitizers were obtained from Baker Chemical Co. The photosensitized irradiation of the samples in benzene were carried out in a Rayonet RPR-208, equipped with the appropriate set of lamps. The product ratios were determined by g.l.c. analysis on a copper column (5 m, diam. 6 mm, 3% SE-30 on Chromosorb W, 45—60 mesh, 120°, 80 ml He min^{-1}).

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[8] P. S. Engel and B. M. Monroe, in 'Advances in Photochemistry,' J. N. Pitts, jun., G. S. Hammond, and W. A. Noyes, jun., Wiley–Interscience, New York, 1971, vol. 8, pp. 273*ff*.

[9] A. A. Lamola and N. J. Turro, 'Energy Transfer and Organic Photochemistry,' Interscience, New York, 1969, p. 38.

[10] B. Stevens, in ref. 8, p. 161; M. Ottolenghi, *Accounts Chem. Res.*, 1973, **6**, 153.

[11] H. Cerfontain and J. A. J. Geenevasen, to be published.

[12] A. van Wageningen, A. A. M. Roof, and H. Cerfontain, *Synth. Comm.*, 1975, **5**, 217.