Photochemistry of Non-conjugated Dienones. Part IV.[1] Photolysis and Thermolysis of Some Retro-α-ionones and Retro-α-ionols

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The isomerizations of (*E*)-retro-α-ionone and a series of methylated and demethyl analogues and some corresponding ionols on direct photolysis and on triplet sensitization have been studied. The direct photolysis of the retro-α-ionones with λ 300 nm leads to 1,3- and 1,5-acyl migration; with λ 254 nm in addition substantial (*Z*)–(*E*)-isomerization is observed. On prolonged irradiation the 1,5-acyl shift product is in some cases eventually converted into the 1,3-acyl shift product. Triplet sensitized reactions lead exclusively to (*Z*)–(*E*)-isomerization; no oxa-di-π-methane-type rearrangement products are found. The different types of photochemical isomerizations of the retro-α- and retro-γ-ionones on direct photolysis can be correlated with the stereochemical configuration of their hepta-4,6-dien-2-one system. The photolysis of the retro-α-ionols leads to (*Z*)–(*E*)-isomerization. Thermolysis of (*E*)-retro-α-ionone in decalin at 150° leads to (*Z*)-α-ionone and (*E*)-β-ionone as primary products. The former product slowly isomerizes to (*E*)-α-ionone which is thermally stable.

As part of the research programme in the field of ionones [2] it was thought of interest to study the photolytic and thermal behaviour of some retro-α-ionones, as model compounds in the series of βγ–δε-unsaturated ketones. For comparison, the photolysis of three corresponding ionols was also studied. In a preliminary account [3] we reported that prolonged photolysis of an ethanolic solution of (*E*)-α-ionone (the photoprecursor of retro-α-ionone [4]) leads to formation of two isomeric products, 3-acetyl-2,4,4-trimethyl-3-vinylcyclohexene and 6-acetyl-1,3,3-trimethyl-2-vinylcyclohexene, which are formed by a 1,3- and a 1,5-acyl shift respectively.

RESULTS

Photolysis of Retro-α-ionones.—Direct photolysis of the (*E*)-retro-α-ionones (1a—d) with 254 or 300 nm radiation leads mainly to the formation of the 1,3-acyl shift products (3a—d); the total amount of by-products in each case is $\leqslant 10\%$. Photolysis of (1e—g) yields both the 1,3- and 1,5-acyl shift products (3e—g) and (4e—g), respectively. With (1e and f), the 1,5-acyl shift product is the main initial product. With (1e) the 1,5-product disappears rapidly to form the 1,3-compound, the only final photoproduct. The photoconversion of the 1,5- into the 1,3-acyl product is slower for (1f) than for (1e). With (1g) the ratio of the 1,3- and 1,5-acyl shift product is independent of the time of irradiation with a value of 0·60 ± 0·02. This value is higher than the initial 1,3- to 1,5-product ratio values for (1e and f) (Figure B, *cf.* Table 1).

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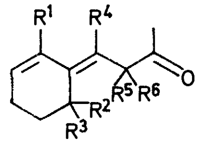
[1] Part III, A. van Wageningen and H. Cerfontain, *Tetrahedron Letters*, 1972, 3679.

[2] Th. J. de Boer, H. A. van't Hof, and J. U. Veenland, *Rec. Trav. chim.*, 1964, **83**, 689; H. A. van't Hof, Thesis, University of Amsterdam, 1966; B. C. Roest, J. U. Veenland, and Th. J. de Boer, *Tetrahedron*, 1967, **23**, 3071; B. C. Roest, Thesis, University of Amsterdam, 1968; Th. J. de Boer, H. A. van't Hof, and J. U. Veenland, *Tetrahedron*, 1967, **23**, 3757.

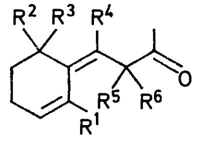
[3] A. van Wageningen and Th. J. de Boer, *Rec. Trav. chim.*, 1970, **89**, 797.

[4] G. Büchi and N. C. Yang, *Helv. Chim. Acta*, 1955, **38**, 1338; M. Mousseron-Canet, M. Mousseron, and P. Legendre, *Compt. Rend.*, 1961, 252, 3928, *Bull. Soc. chim. France*, 1961, 1509.

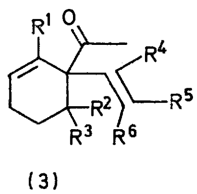
Direct photolysis of the (*Z*)-retro-α-ionones leads qualitatively to the same initial and final photoproducts as observed with the (*E*)-isomers. For example, the ratio of the photoproducts (3g) to (4g) is the same for the photolysis of (2g) and (1g) (Table 1). Further the sample of 4-(6-methylcyclohex-2-enylidene)butan-2-one (1c + 2c) which consisted of a roughly equal mixture of the (*E*)- and (*Z*)-isomer yielded of necessity the same 1,3-acyl shift product (3c).



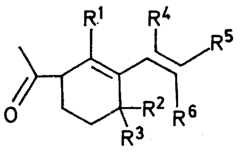
(1) (*E*)-series



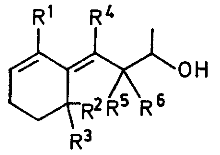
(2) (*Z*)-series



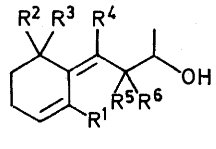
(3)



(4)

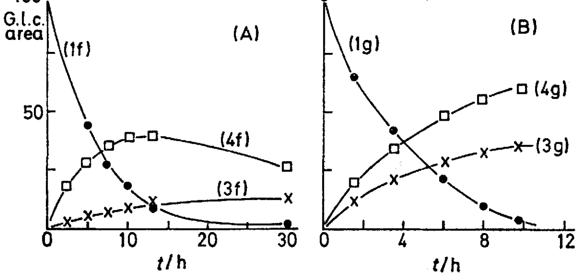


(5)



(6)

a; $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$
b; $R^1 = Me, R^2 = R^3 = R^4 = R^5 = R^6 = H$
c; $R^2 = Me, R^1 = R^3 = R^4 = R^5 = R^6 = H$
d; $R^4 = Me, R^1 = R^2 = R^3 = R^5 = R^6 = H$
e; $R^1 = R^2 = R^3 = Me, R^4 = R^5 = R^6 = H$
f; $R^1 = R^2 = R^3 = R^5 = Me, R^4 = R^6 = H$
g; $R^1 = R^2 = R^3 = R^5 = R^6 = Me, R^4 = H$



Photolysis of the retro-α-ionones (1f) (A) and (1g) (B) in ethanol at λ 300 nm

The initial, zero-time extrapolated ratios of the 1,3- and 1,5-acyl shift products in the photolysis of the retro-α-ionones are collected in Table 1.

In the photolysis at 300 nm of (1f), (1g), (2f), and (2g) small amounts (*ca.* 2%) of the geometric isomers, *i.e.* (2f), (2g), (1f), and (1g) respectively, were also found in the reaction mixture, indicating (*Z*)–(*E*)-isomerization in addition to acyl migration. With 254 nm radiation, the amount of (*Z*)–(*E*)-isomerization becomes of the same order of magnitude as the amount of acyl migration. The rate of photoconversion of (1g) with λ 300 nm is about three times that of (2g). There is some polymer formation with (2g) and almost none with (1g). The polymer formation increases in the order (1g) (*ca.* 0) < (1f) (*cf.* Figure). The lower rate of photoconversion of (1g) compared with (2g) is due mainly to its lower ε (at 300 nm $\varepsilon_{(1g)}$ 35 and $\varepsilon_{(2g)}$ 120 $l\ mol^{-1}\ cm^{-1}$).

TABLE 1

Photokinetically controlled acyl shift product distribution in the photolysis of retro-α-ionones

Substrate	Solvent	λ (nm)	Acyl shift product (%)	
			1,3	1,5
(1a–d)	Ethanol	254	>95	<5
(1e)	Ethanol [a]	254	12 ± 5	88 ± 5
(1f)	Ethanol	300	6 ± 3	94 ± 3
	Acetone	300	6 ± 3	94 ± 3
(1g)	Ethanol	300	37 ± 2	63 ± 2

[a] Similar results were obtained using propan-2-ol, acetone, benzene, or cyclohexane as solvent.

Irradiation of (2g) at 300 nm in carbon tetrachloride as a radical scavenger solvent yielded the same two acyl shift products as in ethanol (only the relative amounts of the minor products were reduced).

Photolysis of the Acyl Shift Products.—Upon irradiation of the 1,3-acyl shift products (3a—f) proper under the same conditions as applied for the retro-α-ionones no monomeric photoproducts were found.

Photolysis of the pure 1,5-acyl shift products (4e and f) at both 254 and 300 nm leads to the formation of the 1,3-acyl shift products (3e and f) respectively with trace amounts of (1e) (*ca.* 2%) and (1f) (*ca.* 2%) respectively. On the other hand photolysis of (4g) (300 nm) does not yield new monomeric products. The photostability of (4g) is due mainly to the low value of ε (at 300 nm $\varepsilon_{(4g)}$ 30 *versus* $\varepsilon_{(4f)}$ 120 and $\varepsilon_{(4e)}$ 275 $l\ mol^{-1}\ cm^{-1}$).

The rate of polymer formation is of the same order of magnitude for the 1,3- and the 1,5-acyl shift product. The lower reactivity of the former as compared with the latter isomer is the result of the lower ε at the wavelength of irradiation (*cf.* Table 6).

Photosensitized Reactions.—Irradiation of the retro-α-ionones (1f and g) in ethanol in the presence of triplet sensitizers with λ 350 nm leads only to (*E*)–(*Z*)-isomerization, and eventually a photostationary (*Z*)–(*E*)-composition is obtained (Table 2). No reaction is observed with pyrene as sensitizer. The photostationary (*Z*) : (*E*) ratio is smaller for (1f) than for (1g).

TABLE 2

Photosensitized (*Z*)–(*E*)-isomerization of the retro-α-ionones (1f and g)

Sensitizer	Triplet energy [a]	Photostationary state (2 : 1) [b]	
		f	g
Pyrene	48·7	*c*	*c*
Benzil	53·7	1·0 ± 0·1	3·9 ± 0·1
1-Acetonaphthone	56·4	2·0 ± 0·1	
2-Acetonaphthone	59·3	2·3 ± 0·1	
Phenanthrene	62·2	2·3 ± 0·1	4·5 ± 0·1
Thioxanthone	65·5	1·6 ± 0·1	
Fluorene	67·6		1·8 ± 0·3
Benzophenone	68·5	1·55 ± 0·05	2·3 ± 0·2
Xanthone	74·2	1·6 ± 0·1	1·65 ± 0·05

[a] A. A. Lamola and N. J. Turro, 'Energy Transfer and Organic Photochemistry,' Interscience, New York, 1969, p. 92. [b] (2) : (1) = *Z* : *E*. [c] No photoisomerization was observed.

The triplet sensitized reaction of (*E*)-retro-α-ionone (1e) could not be studied, as this compound and its geometric isomer are both unstable under the mildest thermal conditions required for satisfactory g.l.c. analysis.

(Z)–(E)-*Photoisomerization of Retro-α-ionols.*—Direct photolysis of retro-α-ionols at λ 254 nm leads to (*Z*)–(*E*)-isomerization and eventually a photostationary state is obtained (Table 3).

TABLE 3

U.v. data and (*Z*)–(*E*)-photoisomerization (λ 254 nm) of retro-α-ionols

Retro-α-ionol	U.v.[a] $\lambda_{max.}$ (nm)	ε (l mol^{-1} cm^{-1})	$\varepsilon_{(6)}/\varepsilon_{(5)}$ [b]	Photo-stationary state (6) : (5) [b]
(5e)	237	13,700		0·9
(5f)	238	18,200	1·4	0·9
(6f)	237	13,100		
(5g)	238	16,200		
(6g)	233	11,300	1·4	2·2

[a] In ethanol as solvent. [b] (6) : (5) = (*Z*) : (*E*).

Thermolysis.—(*E*)-Retro-α-ionone (1e), in contrast to the other retro-α-ionones, is relatively unstable at temperatures >125°. Upon heating (1e) at 150° a rapid conversion into both (*E*)-β-ionone (7) and (*Z*)-α-ionone (8) is observed. Upon prolonged heating (*E*)-α-ionone (9) is also found. This compound arises from (*Z*)–(*E*)-isomerization of (8), since heating of pure (8) does produce (9) as the sole monomeric product. Heating of (*E*)-α-ionone (9) at 150° does not lead to the formation of monomeric products.

Spectral Data and Products Assignments.—The i.r., Raman, and u.v. spectral data of the retro-α-ionones and retro-α-ionols are listed in Tables 4 and 5 respectively. The ^{1}H n.m.r. and mass spectral data of the retro-α-ionones have been deposited as Supplementary Publication No. SUP 21122 (8 pp.).* The (*Z*)- and (*E*)-assignments were made on the basis of Raman and n.m.r. NOE data.

TABLE 4

I.r., Raman, and u.v. data of retro-α-ionones

Retro-α-ionone	I.r. $\nu_{C=O}$ (cm^{-1})	Raman [a] $\nu_{C=C}$ (cm^{-1})	U.v. [b] $\lambda_{max.}$ (nm) Obs.	Calc.[c]	ε (l mol^{-1} cm^{-1})
(1a)	1705	1644	235	234	18,450
			277		1010 [d]
(1b)	1710	1643	238	239	19,700
			285		1180 [d]
(1c + 2c)	1710	1644	235	234	25,200
			274		2500 [d]
(1d)	1705	1634	239	239	15,000
			280		2000 [d]
(1e)	1715	1613	240	239	19,600
		1637	285		340 [d]
(1f)	1705	1605	237	239	17,200
		1638	280		1330 [d]
(2f)	1705	1637	238	239	10,300
			280		1300 [d]
(1g)	1700	1582	239	239	9200
		1630	280		1540 [d]
(2g)	1700	1648	236	239	11,200
			280		720 [d]

[a] Pure liquid. [b] In ethanol as solvent. [c] H. H. Jaffé and M. Orchin, 'Theory and Application of Ultraviolet Spectroscopy,' Wiley, New York, 1962, p. 258. [d] Shoulder on the π–π* absorption.

For most of the retro-α-ionones and the corresponding ionols the observed positions of the u.v. diene maxima at short wavelength are in accordance with the calculated ones (Tables 4 and 5), confirming the coplanarity of the diene system. For the f and g series the observed $\lambda_{max.}$ values are somewhat smaller than the calculated ones, especially in the (*Z*)-compounds, indicating deviation from coplanarity due to methyl repulsion. The high ε values for the carbonyl maxima of the retro-α-ionones (Table 4) illustrate carbonyl–diene interaction, as was also observed with the retro-γ-ionones.[5a]

TABLE 5

I.r. and u.v. data of retro-α-ionols

ionol	I.r.[a] ν_{OH} (cm^{-1})	$\nu_{HC=}$ (cm^{-1})	U.v.[b] $\lambda_{max.}$ (nm) Obs.	Calc.[c]	ε (l mol^{-1} cm^{-1})
(5e)	3400	830	237	239	13,700
(6e)	3400	830			
(5f)	3400	810	238	239	18,200
(6f)	3450	820	237	239	13,100
(5g)	3450	850	238	239	16,200
(6g)	3450	830	233	239	11,300

[a] Pure liquid. [b] In ethanol as solvent. [c] See note *c* of Table 4.

The assignment of the structures of the photoproducts was based on the detailed spectrometric data. The i.r., Raman, and u.v. data are in Table 6. The ^{1}H n.m.r. and mass spectral data have also been deposited in Supplementary Publication No. SUP 21122.* Noteworthy is the blue shift of the u.v. short wavelength absorption of the 1,5-acyl shift products on going from (4e) *via* (4f) to (4g) (Table 6). This may be explained in terms of increasing deformation of the diene system from coplanarity due to increasing mutual repulsion of the methyl groups of the cyclohexadienyl ring and the vinyl side chain.

TABLE 6

I.r., Raman, and u.v. data of the photoproducts of retro-α-ionones

Acyl shift products 1,3	1,5	ν (cm^{-1}) C=O	C=C	HC=	U.v.[b] $\lambda_{max.}$ (nm)	ε (l mol^{-1} cm^{-1})
(3a)		1700vs	1650w	925s	279	280
			1630w			
(3b)		1705vs	1660w	910s	280	70
			1630w			
(3c)		1705vs	1645w	915s	285	170
			1630w			
(3d)		1700vs	1670w	905s	290	170
			1630w			
(3e)		1690vs	1655w	925s	275	40
			1625w			
(3f)		1695vs	1655w	985s	280	130
	(4e)	1700vs		920s	228	4970
					285	155
	(4f)	1705vs	1655w	965s	225	5650
					280	240
	(4g)	1750vs	1650w		215	7400
					280	390

[a] Pure liquid. [b] In ethanol as solvent.

The mass spectra of (*E*)- and (*Z*)-α-ionone, the thermal products of (*Z*)-retro-α-ionone, have been reported.[6] The

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue. Items less than 10 pp. are supplied as full-size copies.

[5] A. van Wageningen, Thesis, University of Amsterdam, 1973, (*a*) pp. 44 and 45; (*b*) p. 30; (*c*) pp. 51—53; (*d*) p. 52.

[6] A. van Wageningen, H. Cerfontain, and N. M. M. Nibbering, *Rec. Trav. chim.*, 1974, **93**, 43.

i.r., u.v., and n.m.r. data of (*Z*)-α-ionone are in Table 7, those of (*E*)-α- and (*E*)-β-ionone are available.[7]

TABLE 7

I.r., u.v., and ^{1}H n.m.r. data of (*Z*)-α-ionone

	U.v.[b]		^{1}H n.m.r.[c]		
			δ[d]		
ν (cm^{-1}) [a]	$\lambda_{max.}$ (nm)	ε (l mol^{-1} cm^{-1})	Me	H	*J*(Hz)
C=O 1690vs	233	10,500	a 0·82 (s),		$J_{f,g}$ 11
			0·91 (s)		
			b 1·52 (m)		$J_{f,h}$ 11
C=C 1610m			c 2·14 (s)		
				d 1·1—1·3 (m)	
				e 1·9—2·2 (m)	
				f 5·71 (dd)	
				g 6·16 (d)	
				h 3·77 (d)	
				i 5·37 (m)	

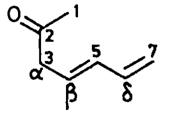
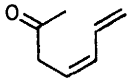
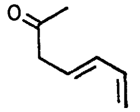
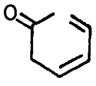
[a, b] See notes to Table 3. [c] s = Singlet, d = doublet, m = multiplet. [d] For assignments, see ref. 5*b*.

DISCUSSION

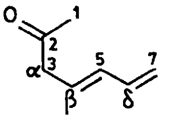
Direct photolysis of the retro-α-ionones at λ 300 nm leads mainly to 1,3- and 1,5-acyl shift isomerizations and to a small extent to (*Z*)-(*E*)-isomerization. The relative amount of geometric isomerization is much greater for irradiation at 254 than at 300 nm. The triplet sensitized reactions of the retro-α-ionones only lead to (*Z*)-(*E*)-isomerization. Accordingly the acyl shift isomerizations occur from the singlet excited state.

TABLE 8

Configurations of the βγ–δε dienone system

Configuration				
βγ-Orientation	*E*	*Z*	*E*	*Z*
γδ-Orientation	single-*E*	single-*E*	single-*Z*	single-*Z*
Type	(*E*)-(*s*-*E*)	(*Z*)-(*s*-*E*)	(*E*)-(*s*-*Z*)	(*Z*)-(*s*-*Z*)
Example	(1e)	(2f)	(*E*)-Retro-γ-ionone	(*Z*)-Retro-γ-ionone

The difference in chemical behaviour of the excited singlet and triplet state of a retro-α-ionone, *i.e.* a βγ–δε-dienone, may be explained qualitatively by analogy with the reasoning advanced by Houk *et al.*[8] for the more simple βγ-enone. The MOs of hepta-4,6-dien-2-one, the simplest βγ–δε-dienone, may be constructed from the MOs of acetone and 1,3-pentadiene. The three highest occupied MOs are obtained by mixing the $n(2p_0)$ orbital of acetone with the bonding π orbitals of the diene, and the three lowest unoccupied MOs by mixing the π*(CO) orbital of acetone with the two anti-bonding π* of the diene.[9] From a comparison with the MO picture of hex-4-en-2-one [10] it seems likely that the lowest excited ***singlet*** state of hepta-4,6-dien-2-one is reached by an electronic transition to the third or second unoccupied MO $({}_4\pi^*_{CO} - \pi^*_{CO} - {}_3\pi^*_{CO}$ and ${}_4\pi^*_{CO} + \pi^*_{CO} - {}_3\pi^*_{CO}$ respectively) which both exhibit, in contrast to the highest occupied orbital $({}_1\pi_{CC} - n_{CO} - {}_2\pi_{CC})$, no C(2)–C(3) bonding. The former MO is weakly C(2)–C(7) and to a lesser extent C(2)–C(5) bonding, while the latter MO is weakly C(2)–C(6) and to a lesser extent C(2)–C(4) bonding. The observed 1,3- and 1,5-acyl shifts then imply that the first excited singlet state involves an electron transfer mainly to the third unoccupied MO. In the absence of configuration interaction calculations this conclusion is only tentative.



As to the ***triplet*** sensitized (*Z*)-(*E*)-isomerizations, the treatment of Houk *et al.*[8,10] predicts that there should be two low-lying excited triplets. One of these would exhibit typical diene triplet reactions, notably (*Z*)-(*E*)-isomerization, cyclobutene formation, and dimerization.[8b] In the other triplet state there should occur weak C(2)–C(4) bonding, which could be the driving force for an oxa-di-π-methane rearrangement,[11] and weak C(2)–C(7) bonding which could lead to the 1,5-acyl shift product. The retro-α-ionones (1f and g) and (2f and g) upon triplet photosensitization only exhibit geometric isomerization [as do the corresponding ionols on direct irradiation (Table 3)] and no oxa-di-π-methane rearrangement. The cyclobutene formation on direct irradiation of (*E*)-retro-γ-ionone [12] is thus probably a diene triplet reaction.

The degree of (*Z*)-(*E*)-isomerization in the direct photolysis of the retro-α-ionones (1e—g) and (2e—g) is almost negligible at 300 nm, but very substantial for 254 nm radiation. This may be explained by considering two excited singlet states. Photolysis at 300 nm leads to population of the lowest excited singlet state for which the 1,3- and 1,5-acyl shift reactions are fast relative to intersystem crossing. At 254 nm, however, the second excited singlet state is populated and this undergoes both internal conversion to the lowest excited singlet state and intersystem crossing to the triplet states, of which the diene state exhibits (*Z*)-(*E*)-isomerization.

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[7] E. T. Theimer and S. Lemberg, *Proc. Sci. Sect. Toilet Goods Assoc.*, 1961, no, 35, 18; H. A. van 't Hof, Thesis, University of Amsterdam, 1964, p. 16.

[8] (*a*) K. N. Houk and D. J. Northington, *J. Amer. Chem. Soc.*, 1972, **94**, 1387; (*b*) K. N. Houk, personal communication.

[9] R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1.

[10] K. N. Houk, D. J. Northington, and R. E. Duke, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 6233.

[11] S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531.

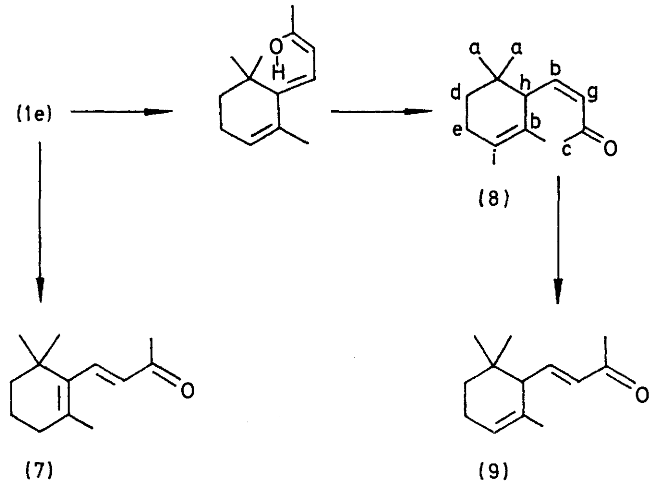
[12] A. A. M. Roof, A. van Wageningen, C. Kruk, and H. Cerfontain, *Tetrahedron Letters*, 1972, 367.

In the series of retro-α-ionones four possible configurations of the dienone system must be considered (Table 8). From the present and other results [1,5c,12] it appears that there is a correlation between the dienone configuration and the type of reaction on direct photolysis. Compounds of the type γδ-(*s*-*E*) all undergo acyl shift reactions, whereas the γδ-(*s*-*Z*) compounds undergo [2 + 2] cycloaddition. For instance, the retro-α-ionones yield 1,3- and 1,5-acyl shift products (Table 1), whereas (*E*)- and (*Z*)-retro-γ-ionone undergo cycloaddition with formation of a cyclobutene [12] and a tricyclic oxetan respectively. Cyclobutene formation from the (*E*)-isomer is favoured, because of release of steric strain due to interaction between the carbonyl-containing side chain and the geminal dimethyl group at the cyclohexene ring. By contrast, the carbonyl-containing side chain of the (*Z*)-isomer prohibits the cyclobutene formation, because of repulsive steric interaction with the exocyclic methylene group. This interaction in fact places the carbonyl and the exocyclic methylene groups in a mutual favourable position to form the tricyclic oxetan by intramolecular $[2\pi_{CO} + 2\pi_{CO}]$ cycloaddition.

The differences in the ratio of the 1,3- and 1,5-acyl shift products formed in the direct photolysis of the retro-α-ionones (1a—g) are very significant (Table 1). The predominant 1,3-acyl shift observed with the retro-α-ionones (1a—d) can be explained in terms of the spatial configuration of the third highest unoccupied obtital (see above), if it is further assumed that the 1,5-shift, which is also symmetry allowed, does not take place for geometric reasons. Accordingly, it is proposed that the diene configuration of the lowest excited singlet state has a planar transoid diene structure. With (1e), (1f), and (2f), the 1,5-shift product dominates over the 1,3-one. This may be explained in three ways. First C-3 may be shielded by the two methyls of the geminal dimethyl system, thus rendering the 1,3-acyl shift less probable. Secondly in the lowest excited singlet state of these substrates the C(3)–C(7) carbon chain may be distorted so far from coplanarity * as to make the concerted 1,5-shift relatively more attractive than the 1,3-shift. Thirdly, the 1,5-acyl shift may proceed by α-cleavage and subsequent radical recombination, as was established, *e.g.*, by βγ-unsaturated aryl ketones.[13] Since the use of CCl_4 does not inhibit the acyl isomerisations of (2g), the 1,5-acyl shift must then, however, proceed *via* an intimate radical pair. Finally, the lower 1,5- to 1,3-isomer ratio for (1g) as compared with those for (1e and f) may be explained by overcrowding in the transition state leading to the 1,5-shift product (4g), rendering its formation less likely.

As regards geometric isomerization of the retro-α-ionones and -ionols the following aspect deserves attention. The dependence of the photostationary *Z*:*E*-ratio on the triplet energy of the photosensitizer observed for the retro-α-ionones (Table 2) is similar to, *e.g.*, the piperylenes [14] 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. This dependence may therefore be explained along similar lines as proposed for the piperylenes.[15] The limiting *Z* : *E*-value at high triplet energy is the same for the f and g series. The higher *Z* : *E*-values observed at lower triplet energy may be explained in terms of a lower efficiency for triplet energy transfer to the *Z*- compared with the *E*-isomer. The higher *Z* : *E*-ratio of the g series relative to that of the f then leads to the inference that the triplet energy transfer efficiency to the *Z*-isomer is lower in the case of the g than of the f series, probably for steric reasons. The lower value of $\lambda_{max.}$ of (2g) compared with both the calculated one and that of (2f) (Table 2) does indicate steric strain in (2g).

Thermolysis of (E)-*Retro-α-ionone* (1e).—The conversion of (1e) into (*Z*)-α-ionone (8) may be explained by ionic enolization of (1e) and a subsequent symmetry allowed [16] [1,5] shift of the hydroxy hydrogen atom. The alternative explanation, *viz.* a one-step [1,3] shift of one of the methylene hydrogens adjacent to the carbonyl group, seems unlikely as the suprafacial sigmatropic 1,3-hydrogen shift is symmetry forbidden and the antarafacial one geometrically unfavourable in thermal reactions.[16] Moreover, this would in all probability lead to a mixture of both (*Z*)- and (*E*)-α-ionone, whereas in fact only the (*Z*)-isomer is formed. For the conversion of (1e) into (*E*)-β-ionone (7) three routes may be envisaged. First two subsequent [1,3] hydrogen shifts with (*E*)- and/or (*Z*)-α-ionone as (the) intermediate(s) take place; secondly a one-step [1,5] hydrogen shift occurs; and thirdly enolization of (1e) and a subsequent [1,7] shift of the hydroxy hydrogen



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[*] The observed deviation between the observed and calculated $\lambda_{max.}$ for these substrates (Table 4) is in line with this supposition.

[13] H.-U. Gonzenbach, K. Schaffner, B. Blank, and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1741.

[14] 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.

[15] N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, 1965, p. 179; P. J. Wagner and G. S. Hammond, 'Advances in Photochemistry,' Interscience, New York, 1968, vol. 5, p. 80.

[16] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, pp. 114*ff.*

atom in the ' single (Z) ' diene conformation of the enol takes place. The first two routes are considered to be unlikely, since for thermal reactions [1,3] hydrogen shifts are symmetry forbidden, and [1,5] hydrogen shifts seem to be allowed only in *cisoid* diene systems.[16] According to model studies, the [1,7] hydrogen shift in the third route is not a very likely process either. The formation of (E)-β-ionone from (E)-retro-α-ionone is therefore unexplained.

The thermal stability is very much greater for (1f and g) than for (1e). This is understandable on the basis of the proposed first step for the thermal conversion of (1e), *viz.* the ionic enolization. This enolization cannot take place for (1g), and with (1f) the formation of the intermediate enolate anion will be more difficult in view of the additional electron-donating methyl group.

TABLE 9

G.l.c. columns and conditions

	Column				Solid support				
Substrate	Material	Length (m)	ϕ (mm)	Adsorbent (wt %)	Material	Particle size (mesh)	Temp. (°C)	He flow rate (ml min^{-1})	Retention time order
(1a)	Glass	3·5	6	Reoplex 400 (15)	Chromosorb W	40—60	185	125	(3a) < (1a)
(1b), (1c + 2c)	Brass	1·0	6	Reoplex 400 (15)	Kieselguhr	42—60	155	200	(3b) < (1b); (3c) < (1c + 2c)
(1d)	Brass	1·0	6	Apiezon L (15)	Chromosorb A	45—60	140	60	(3d) < (1d)
(1e)	Brass	2·5	6	Carbowax 20M (7·5)	Kiesel guhr	42—60	90	150—200	(4e) < (3e) < (1e)
(1f); (2f)	Glass	3·5	6	Reoplex 400 (15)	Chromosorb P	40—60	145	100—120	(3f) < (2f) < (4f) ⩽ (1f)
(1g), (2g)									(2g) < (4g) < (3g) ⩽ (1g)
(2g)	Glass	5·0	6	Reoplex 400 (15)	Chromosorb P	40—60	160	120	(2g) < (4g) < (3g) ⩽ (1g)
(5e), (5f), (6g)	Brass	1·5	6	Carbowax 20M (5)	Chromosorb A	45—60	120	120	(6e) ⩽ (5e), (6f) ⩽ (5f), (6g) ⩽ (5g)

EXPERIMENTAL

Materials.—The synthesis of the retro-α-ionones has been described elsewhere.[17] The retro-α-ionols were obtained from the corresponding ionones by reduction with RedAl (Aldrich), as described for β-ionol.[5d,18]

Photolyses.—Ethanolic solutions of the retro-α-ionones and -ionols (2·5% v/v) in quartz reaction vessels were photolysed in a Rayonet reactor at λ 254, 300, or 350 nm at 30° in the absence or presence or suitable photo-sensitizers to the desired conversion. The mixtures were then concentrated by removing >90% of the ethanol by rotary evaporation and separated into the components by g.l.c., using He as carrier gas. The specifications of the semianalytical columns and the analysis are given in Table 9. The components were identified spectrometrically.

The progress of the photolyses was monitored by sampling at appropriate reaction times, and subsequent g.l.c. analysis on the same semianalytical columns. The amounts of starting material and photoproducts shown in the Figure are the g.l.c. peak areas.

Thermolyses.—The thermolyses of (Z)-retro-α-ionone were carried out by heating a sample (250 mg) as such, or in decalin (0·5 ml), at 150°.

Spectral Identification.—The i.r. spectra were recorded from the pure components on a Unicam SP 200 or a Beckman IR 18A spectrometer. The Raman spectra were obtained with a Coderg PH 1 spectrometer using a CRL 52 Mg laser. The u.v. spectra were recorded on a Shimadzu UV 200 or a Beckman DB-GT spectrometer. The ^{1}H n.m.r. spectra were recorded from dilute CCl_4 solutions (5—10%) with tetramethylsilane as internal standard on Varian HA 100 or A 60 spectrometers. The mass spectra were obtained with a Varian-MAT 711 mass spectrometer at 70 eV.

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