Stereospecific Photochemical Rearrangements of Chiral Cyclohexenones

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Summary The stereospecificity of the photorearrangements of monocyclic chiral 4,4-disubstituted cyclohexenones has been studied; no racemization has been found in either the Type A or aryl migration pathways.

We recently reported the photorearrangement of (**1a**) to (**2a**) and (**3a**) to be largely, if not totally, stereospecific.[1] The large limits of uncertainty (*ca.* 10%) were due to the small optical purity of (**1a**) and the method used to determine the optical purities [using the chiral ^1H n.m.r. shift reagent Eu(hfc)$_3$], and represent the maximum reaction *via* non-synchronous mechanisms.[2] We now report the results of experiments using (**1a**) of higher optical purity, and (**1b**) of even greater optical purity. In the latter system, one observes aryl migration products, as well as Type A[3] photoproducts, depending on the solvent.[4] Some of the data obtained are shown in the Table.

TABLE

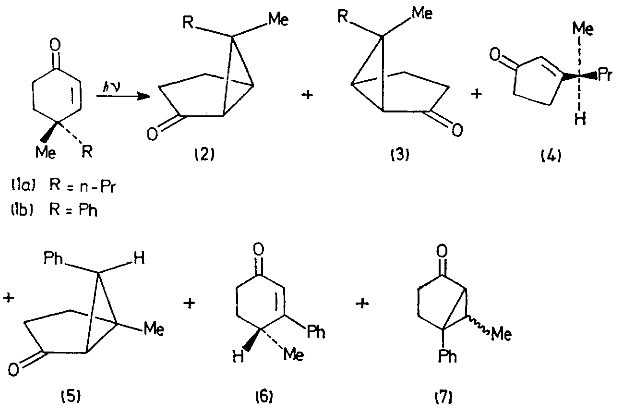
Compound	Optical rotation, $[\alpha]_D^{25}$	Optical purity, %
(**1a**) (starting)	(+) 11·93 ± 0·01°	26·8 ± 1·3
(**1a**) (recovered)^a	(+) 11·89 ± 0·03°	26·4 ± 0·1
(**2a**)^a	(−) 13·13 ± 0·36°	27·2 ± 1·0
(**3a**)^a	(+) 9·96 ± 0·50°	27·5 ± 0·9
(**4**)^a	(+) 7·81 ± 0·07°	> 16·9^b
(**1b**) (starting)	(+) 53·83 ± 0·02°	41·73 ± 0·02
(**1b**) (recovered)^c	(+) 51·25 ± 2·38°	39·73 ± 1·84^d
(**2b**)^c	(−) 4·41 ± 0·98°	41·9 ± 1·5
(**5**)^c	(−) 1·76 ± 0·42°	41·2 ± 1·3

^{a} Photolysis in Bu^{t}OH for 12 h at 254 nm; ^{b} Minimum optical purity from oxidation to α-methylvaleric acid; ^{c} Photolysis in 95% EtOH for 24 h at >300 nm; ^{d} Large error due to small size of recovered sample. No racemization seen after 7 h photolysis.

The optical purity of (**1b**) was determined by polarimetry[5] while that of (**1a**) was determined by oxidation to (**8**) and application of the ^1H n.m.r. chiral shift reagent technique.[1] Optical purities of (**2**), (**3**), and (**5**) were also determined using Eu(hfc)$_3$. Gas-liquid partition chromatography was used to separate compounds, with multiple passes used when necessary to obtain pure material.

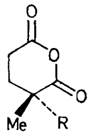
The absolute configurations of (**1a**) and (**1b**) were unambiguously assigned as *R*.[5] The configurations of (**2**), (**3a**) and (**5**) were assigned using the 'inverse octant rule'[6] obeyed by bicyclo[3.1.0]hexan-2-ones. The position of the substituents as *endo* or *exo* had been previously established.[4] The configuration of (**4**) was established as *S* by Kuhn-Roth oxidation[8] to (+)-α-methylvaleric acid (**9**) of known configuration.[9] Experiments to determine the configuration of (**6**) are incomplete. Products (**3b**) and (**7**) from (**1b**)[4] were not isolated in sufficient purity to permit stereochemical assignments.

Rearrangement of (**1b**) to (**5**) proceeds without loss of chirality and with no racemization of (**1b**). A possible intermediate in the formation of (**5**) and (**6**) is (**10**) which would lead to (**6**) with predicted configuration *R*. The rearrangements to (**2**) and (**3**) are at least 99% stereospecific.[10] As postulated,[1] the rearrangement is specific on each face of the ring, giving diastereomeric lumiketones with inversion at the migrating carbon (C-4). Ring opened diradicals such as (**11**)[11] are no longer plausible as intermediates in this reaction, which appears to be a $_\sigma 2_a + _\pi 2_a$ rearrangement.[12] This is despite the fact that the reaction originates from a triplet state[7] (probably $^3\pi,\pi^*$)[4] derived from excitation into either the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ absorption bands of the carbonyl-containing chromophore.

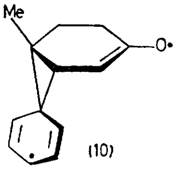


(1a) R = n-Pr
(1b) R = Ph

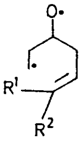
(2) (3) (4) (5) (6) (7)



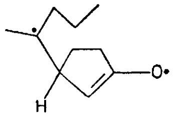
(8)



(10)



(11)



(12)

Diradicals such as (**12**) have been proposed as intermediates in the formation of (**4**) from (**1a**).[7,11a] Diradicals of this type account for epimerization of the lumiketones while maintaining configuration at C-3, and would thus lead to racemization on formation of lumiketones from (**1**). Since this is not the case,[10] we conclude that such diradicals are not formed on photoexcitation of (**1**).[1,10] Formation of (**4**) seems to involve in effect a $_\sigma 2_a + _\sigma 2_a$ cycloaddition mechanism, with simultaneous hydrogen shift and ring contraction.[10]

The quantum inefficiency in these rearrangements[1,3,7] is probably associated with competitive crossing to the ground state potential surfaces of the starting material and the product from relaxed enone triplets with a highly twisted geometry.[13]

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