Photolysis of Steroidal β,γ-Epoxyketones

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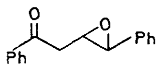
Summary An unusual condensed phase photodecarbonylation of a steroidal 9,10-epoxy-6-ketone is reported in which hydrogen atom shifts from C-7 to C-5 and from C-8 to C-7 give rise to the main product.

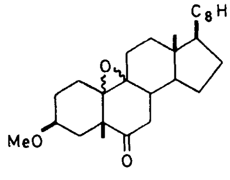
ALTHOUGH the photochemistry of α,β-epoxyketones is well known,[1] that of β,γ-epoxyketones has been little studied.[2] Compound (**1**) gave products derived from Norrish Type II cleavage,[2a] while the second reported example gave no well defined products.[2b] We have examined the photochemical behaviour of the β,γ-epoxyketones (**2**)[3] and (**3**),[4] which are available from successive hydrolysis and oxidation of the appropriate 6β-acetoxy-9,10-epoxides,[4,5] and in which the Norrish Type II cleavage is not possible.

Irradiation† of an ethereal solution of the 9α,10α-epoxyketone (**2**) in an atmosphere of nitrogen resulted in rapid decarbonylation and formation of the unsaturated epoxide (**4**)‡ (20%) and several minor products, one of which was identified as the B-norepoxide (**5**)‡ (3%). Similar irradiation in methanol gave the methyl ester (**6**)‡ (73%), whereas in acetone (**2**) was partially decomposed (recovery 42%) to give essentially polymeric material. Surprisingly, and in contrast to these observations, the 9β,10β-epoxyketone (**3**) remained unchanged on irradiating in ether. In methanol and acetone no well defined products were obtained and the 9β,10β-epoxyketone was recovered unchanged (50 and 44%, respectively).

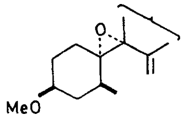
The products obtained from 9α,10α-epoxyketone (**2**) are analogous to those obtained from irradiation of ether solutions of friedelin (**7**),[6] and this work provides another example of the rarely observed photodecarbonylation of simple cyclohexanones in the condensed phase.[2b,7] By analogy with recent mechanistic studies of cyclohexanones,[7] the unsaturated epoxide (**4**) and the B-norepoxide (**5**) are assumed to be formed *via* the diradicals (**a**) and (**b**) (Scheme). The precise mechanism of the conversion of radicals of the type (**b**) into olefins of the type (**4**) has not been previously studied. We present evidence here which indicates that two hydrogen atom migrations, C-7 → C-5 and C-8 → C-7, are involved. The migrations may be consecutive in this order, in which case the carbene (**c**) would be involved, or they may be synchronous, leading directly to the olefin (**4**) (Scheme). The photolysis of (**2**) in methanol obviously proceeds characteristically *via* the keten (**d**) to the ester (**6**) (Scheme). The retention of configuration at C-5 in (**4**), (**5**), and (**6**) may be due to some degree of association of the radical pairs in (**a**) and (**b**). In addition, inspection of models suggests that steric interaction between the 5-methyl group and the 7-methylene group in (**a**) and (**b**) could be an important factor in preventing inversion.



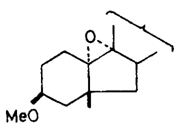
(1)



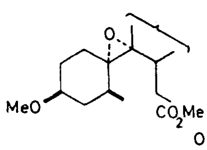
(2) 9α,10α
(3) 9β,10β



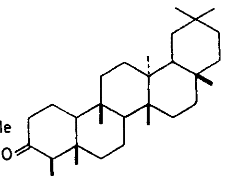
(4)



(5)



(6)



(7)

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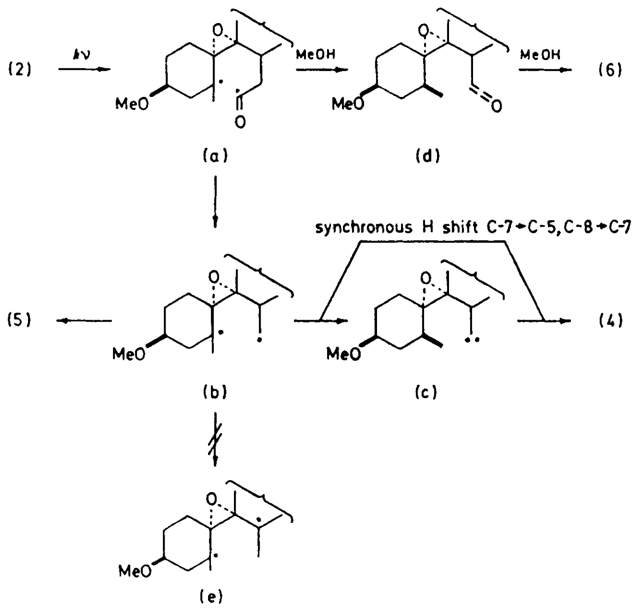
† Medium pressure 125 W Hg lamp; quartz apparatus.

‡ Satisfactory spectroscopic and analytical data have been obtained. In particular, there is good evidence (^1H n.m.r.) for the retention of configuration at C-5.

These mechanistic conclusions are supported by the photolysis, in two separate experiments, of two samples of deuteriated 9α,10α-epoxyketone (**2**)[(A)7,7-$^2H_2$ 88%, 7-$^2H_1$ 9%, $^2H_0$ 3% and (B) 7,7-$^2H_2$ 59%, 7-$^2H_1$ 35%, $^2H_0$ 6%]. M.s. analysis of the unsaturated epoxide (**4**) and the B-nor-epoxide (**5**) which were isolated in each experiment showed that the deuterium content remained unchanged. The 5-methyl group in the two samples of (**4**) appeared essentially as a singlet in the ^1H n.m.r. spectra, showing that mainly deuterium was attached to C-5 and that transfer of hydrogen atoms from C-8 to C-5 in the diradical (**b**) is unimportant. It is generally assumed that such 1,4-hydrogen migrations are important in vapour phase decarbonylations of cyclohexanones.[7] The observed integrated areas of the olefinic proton signals in the ^1H n.m.r. spectra of the two samples of (**4**) [from (A) and (B)] compare well with those calculated assuming the above mechanisms to be correct (Table). No allowance is made for possible kinetic isotope effects which, unless very large, would be difficult to detect accurately in the calculated figures for these mechanisms.



Scheme

Table

Sample	Areas of olefinic signals	
	Integrated	Calculated
(A)	0·98H	1·07H
(B)	1·25H	1·23H

An obvious alternative mechanism involving the diradical (**e**) can be discounted since this would give much smaller integrated areas for the olefinic proton signals, and kinetic isotope effects would be expected to reduce these values even further.

At this stage, no satisfactory explanation for the lack of reactivity of the 9β,10β-epoxyketone (**3**) can be offered. However, it is noteworthy that the base peak in the mass spectrum of (**3**) is the molecular ion, whereas in the spectrum of (**2**) peaks at m/e 412 and m/e 398 have similar intensities to that of the molecular ion. It is apparent that their photochemical reactivity and behaviour in the mass spectrometer are similar, as is the case in certain other systems.[8]

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