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Concerning the Mechanism of a Photochemical Decarbonylation

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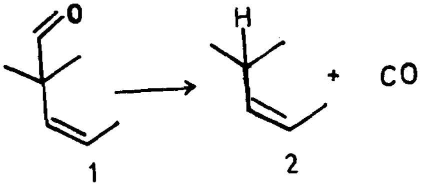
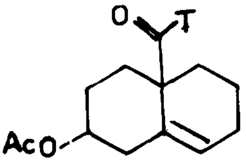
Jeger, Schaffner and co-workers[1] have recently described an elegant light-induced conversion of 3,17-bisethylenedioxyandrost-5-en-19-al into 19-nor-3,17-bisethylenedioxyandrost-5-ene. This is represented in a generalized form in scheme I.



Scheme I

In this communication we describe the mechanism of this transformation which has been studied by photolysing the two aldehydes, 19-oxocholesterol acetate-19-^{3}H (3, partial structure) and 19-oxocholesterol (4, partial structure), in the condensed phase. Our results strongly suggest that this conversion

(1 - 2) takes place predominantly through a concerted intramolecular mechanism. Previously, examples of intramolecular decarbonylation have only been reported in the gas phase.[2]



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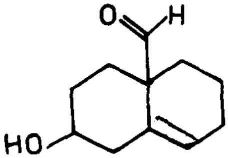

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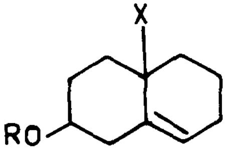


5 R= Ac, X=T

6 R= H, X=H

Irradiation of the tritiated aldehyde (3) in methanol or in benzene gave the corresponding 19-nor derivative (5) in 70% yield. This conversion was attended by a complete retention of radioactivity (Table 1, Expt. a). Irradiation of a mixture of the tritiated aldehyde (3) and the non-tritiated aldehyde (4) gave after separation by chromatography the two 19-nor derivatives (5) and (6). These derivatives completely retained the hydrogen isotopes which were originall present in the parent aldehydes (Table 1, Expts. b and c). These experiments eliminate a 'non-cage' free radical mechanis involving formyl and carbon radicals, for the conversion 1 - 2 (scheme I).[4] A radical-cage mechanism was eliminated by the following experiments. The theory of 'cage' dissociation process as formulated by Noyes suggests that the probability of escape from the solvent 'cage' should increase with temperature because of the decrease in density and viscosity of the medium.[5] Irradiation of a mixture of the aldehydes (3) and (4), in boiling toluene, gave the two 19-nor derivatives (5) and (6); cross-products could not be detected in this experiment (Table 1, Expt. d). Furthermore, in connection with studies on 'cage' reactions, it has been suggested that concentration of a reactive scavenger at 1M may suppress as much as 90% of the geminate recombination.[5,6] A higher limit has been set by Hammond and Waits, these workers have shown that the concentrations of bromine or iodine approaching 1.03M are necessary to suppress as much as 50% of geminate recombination in the decomposition of 1,1 -azocyanocyclohexane.[7]

We have conducted the photolysis of the tritiated aldehyde (3) in the presence of 2.3M thiophenol[a] and have noted no significant loss in the radioactivity of the derived 19-nor compound (5, Expt. f).[b] Although it can be argued that in the event of a 'radical-cage' mechanism as

$$\text{R-CH=O} \longrightarrow (\text{R}^{\bullet} + {}^{\bullet}\text{CH=O}) \longrightarrow \text{RH} + \text{CO}$$

formyl radicals, $\text{H-}\dot{\text{C}}\text{=O}$, being powerful hydrogen donors might exclude the participation of the scavenger, even though the

[a] We are grateful to Professor D.H.R. Barton and Dr. P.G. Sammes for informing us of their experiments which firmly established that thiophenol is a good quencher of carbon radicals.

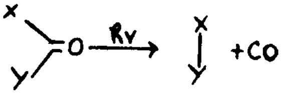
[b] A small loss of radioactivity in experiment (f) can be attributed to a possible competing reaction.[8]

Table 1

Expt.	Photolysis of[a]	Concentration	Solvent	Radioactivity of the derived 19-nor compound[b]
a	3, 20°C	2.27×10^{-3}M	MeOH	1.00
b	3 + 20°C	1 $\times10^{-3}$M	MeOH	1.03
	4	2 $\times10^{-3}$M		0.01
c	3 + 20°C	1 $\times10^{-1}$M	Toluene	0.96
	4	2.5 $\times10^{-1}$M		-
d	3 + at reflux	6.3 $\times10^{-3}$M	Toluene	1.00
	4	7 $\times10^{-3}$M		0.01
e	3, 20°C	2.27×10^{-3}M	Cyclohexane	1.03
f	3 +	7 $\times10^{-2}$M	Toluene	0.93
	thiophenol	2.3 M		-

a. Photolyses were performed in a pyrex vessel using a 200 watt Hanovia high pressure mercury lamp.
b. Error ± 4%

latter is present in very high concentration. However, in view of the hydrogen isotope effect it is highly unlikely that this argument is applicable to T-C=O radicals. These experiments strongly suggest that the transformation 1 - 2 takes place predominantly through a concerted intramolecular mechanism involving a primary photochemical process. This process is represented as:[c,d.]



[c.] This problem is being actively studied in the laboratory of Professor O. Jeger and K. Schaffner. We are grateful to Dr. K. Schaffner for many helpful discussions.

[d.] The involvement of an intramolecular process for the formation of CH$_4$ from CH$_3$CHO has been attributed to a singlet excited state.[2b] It would be interesting to see if in the present case the interaction of the 5,6 double bond with the 19-carbonyl chromophore facilitates decomposition via a singlet state.

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