

PHOTOCYCLOADDITION OF ACETALDEHYDE TO (E)- AND (Z)-PENTA-1,3-DIENE

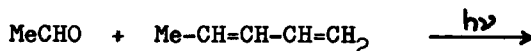
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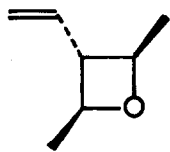
(Received in UK 21 January 1977; accepted for publication 7 March 1977)

Penta-1,3-diene (piperylene)(1) has often been used as a quencher of the triplet excited states of carbonyl compounds, on the assumption that only physical quenching of triplet energy occurs. However, there is an isolated report of chemical reaction involving the photocycloaddition of penta-1,3-diene to a ketone¹. We now wish to report that the photocycloaddition of acetaldehyde to (E)- or (Z)-penta-1,3-diene efficiently leads to the oxetans (2)-(8), and that this reaction provides detailed information on the regioselectivity and stereoselectivity of a photochemical [2+2] addition.

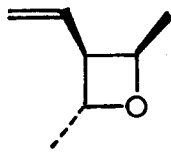
U.v. irradiations (λ ca. 300 nm) of acetaldehyde (1.8 mol l^{-1}) in benzene solution containing either (E)- or (Z)-penta-1,3-diene (1.0 mol l^{-1}) lead to the mixtures of oxetans shown in the Table. The separate oxetans were isolated by preparative g.l.c. and the structural assignments made on the basis of their ¹H and ¹³C n.m.r. spectra, and i.r. spectra.



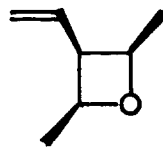
(1)



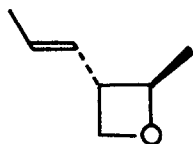
(2)



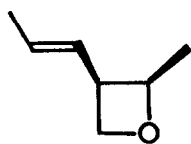
(3)



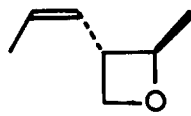
(4)



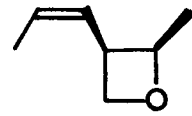
(5)



(6)



(7)



(8)

Table

Diene (1)	Oxetan Product Ratios ^d						
	(2)	(3)	(4)	(5)	(6)	(7)	(8)
(E)-(1)	0.51	0.16	<u>a</u>	0.25	0.08	<u>c</u>	<u>c</u>
(Z)-(1)	<u>b</u>	0.48	0.15	<u>b</u>	<u>c</u>	0.29	0.08
<u>a</u> < 0.02		<u>b</u> < 0.01		<u>c</u> < 0.005		^d Diene isomerisation during reaction < 5%	

These results show several features of the reaction.

- (i) The cycloaddition is highly stereoselective, since either isomer of diene gives more than 97% retention of configuration of diene geometry in the oxetan products.
- (ii) Reaction is clearly regioselective, in contrast to the photocycloaddition of acetone to 2-methylhexa-2,4-diene². It is unusual to find that an attack at the more substituted double bond of penta-1,3-diene is preferred (63-67% in the present case), although this might point to a concerted [2+2] reaction with a small steric demand³.
- (iii) The orientation of addition is such that only 3-enyl oxetans are produced. There is no trace of the 4-enyl oxetan also produced from acetone and buta-1,3-diene⁴.
- (iv) There is a fairly constant preference (76-78%), which is probably steric in origin, for an (E)- arrangement of the diene enyl grouping and the acetaldehyde methyl in the oxetans produced.

In view of the known examples of photochemical additions of ketones with conjugated dienes,^{1,2,4} and of aldehydes with dienes,^{5,6} it is likely that cycloaddition occurs by attack of singlet excited acetaldehyde on ground-state diene, perhaps via an exciplex. Two points support this analogy:

- (a) Photoreactions of ketones with alkenes which involve a triplet intermediate have been shown to occur with substantial loss of stereochemistry⁷, whilst those involving singlet intermediates are generally more stereoselective⁸.
- (b) The known dimers of penta-1,3-diene, which are produced on triplet sensitisation⁹, were noticeably absent in the present reaction. Furthermore, (E)-(Z) isomerisation of the diene was slow in comparison with cycloaddition.

References

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