

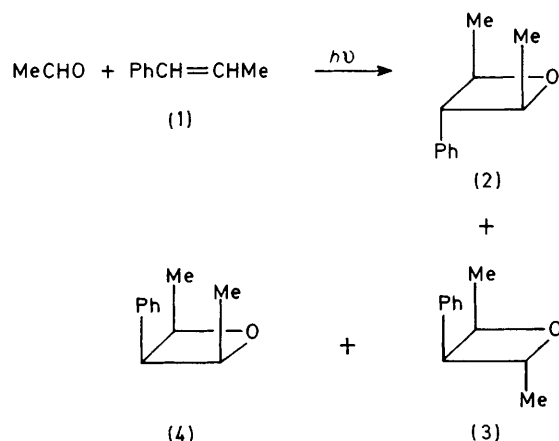
Photochemical Cycloaddition of Aldehydes to Styrenes

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Summary U.v. irradiation of acetaldehyde in the presence of styrene or methylstyrenes yields oxetans in a reaction which is both regio- and stereo-selective; benzaldehyde also reacts, but in a less selective manner.

AMONGST the hundreds of known examples of [2+2] photochemical cycloadditions of carbonyl compounds to alkenes (Paterno-Büchi reaction),¹ there is an isolated example of the reaction of simple carbonyl compounds with styrenes.² We now report that the photocycloaddition of acetaldehyde to styrenes is both regioselective and stereoselective, and we present the first examples of photoaddition of aromatic aldehydes to styrenes.

Irradiation of a solution of acetaldehyde (0.2 mol) and 1-phenylpropene (1) (0.05 mol) in benzene (65 ml) using quartz apparatus and a 450 W medium-pressure mercury arc lamp led to *cis-trans*-isomerisation of the alkene, and the formation of the oxetans (2)—(4) (ca. 60% yield) which were separated by preparative g.l.c. Structures of the adducts (2)—(4) were clearly shown by their ¹H and ¹³C n.m.r. spectra. Reaction appeared to be highly regioselective, since no 3,4-dimethyl-2-phenyloxetans were detected.



Estimating the stereoselectivity of the cycloaddition was made difficult by the concomitant *cis-trans*-isomerisation of the alkene; however, a study of the oxetan yields as a function of irradiation time suggested that the reaction was

highly stereoselective. The relative yields of oxetans formed from irradiations involving each isomer of the alkene (1) (before significant *cis-trans*-isomerisation) are shown in the Table. Thus, the oxetans (3) and (4) are

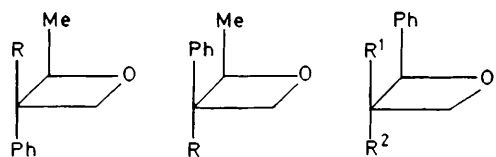
TABLE. Stereoselectivities in the formation of (2)—(4) from acetaldehyde and (1)

Alkene ^a	Oxetan ratio ^b		
	(2)	(3)	(4)
<i>cis</i> -(1)	≤ 0.05	0.57	0.38
<i>trans</i> -(1)	0.78	0.20	≤ 0.02

^a Starting isomeric purity >99%. ^b Determined at ≤4% isomerisation of the alkene (1).

largely formed from *cis*-(1), and at least 95% of the total oxetan product retains the geometry of the *cis*-alkene unit. Conversely, the oxetans (2) and (3) are mainly formed from *trans*-(1) in a reaction which is at least 98% stereoselective. This selectivity is higher than that found in the photo-addition of acetaldehyde to but-2-ene.³

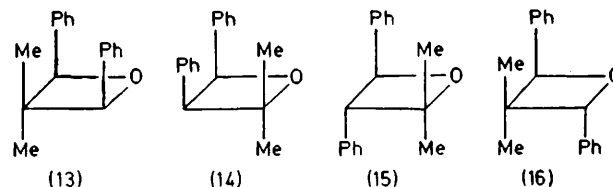
Similar irradiations of acetaldehyde in the presence of styrene gave the oxetans (5) and (6) in the ratio 3.6:1. 2-Phenylpropene yielded the oxetans (7) and (8) in the ratio 1.9:1, and in a total yield of 67%.



- (5) R = H (6) R = H (9) R¹ = Ph, R² = H
 (7) R = Me (8) R = Me (10) R¹ = H, R² = Ph
 (11) R¹ = Ph, R² = Me
 (12) R¹ = Me, R² = Ph

Irradiation of a solution of benzaldehyde and styrene (10 equiv.) in benzene gave, besides polymer, a 1:1 mixture of the *cis*- and *trans*-2,3-diphenyloxetans (9) and (10) which was separated by column chromatography in 31% isolated yield. 2-Phenylpropene (2 equiv.) reacted similarly to

give a 1.5:1 ratio (30% isolated yield) of *Z*- and *E*-oxetans (11) and (12) respectively. 2-Methyl-1-phenylpropene gave a 2:1.3:1 mixture of the oxetans (13), (14) and (15), respectively in 43% yield; the fourth possible stereoisomer (16) was not detected. The stereochemistry of the oxetan (13) is clearly proven as *Z* by its n.m.r. spectrum, which shows two non-equivalent methyl groups, whereas the *E*-isomer (16) has an element of symmetry and would show only one such methyl resonance.



The lack of previous examples of such photocycloadditions may reflect the belief that, because the triplet energy of styrenes (*e.g.* styrene, 61.7 kcal mol⁻¹)⁴ is much lower than that of carbonyl compounds (*e.g.* benzaldehyde, 72 kcal mol⁻¹)⁴, efficient triplet energy transfer from carbonyl compound to styrene will be the exclusive reaction. However, the mechanisms of these reactions of acetaldehyde are likely to involve the singlet excited state of the aldehyde, and addition thus proceeds with high stereoselectivity.^{3,5} In contrast, the very high intersystem crossing rate of aromatic carbonyl compounds ensures that benzaldehyde cycloadditions will occur *via* the triplet state,⁶ in competition with triplet energy transfer. Irradiations at wavelengths >310 nm led to the same products, and under these conditions the singlet excited state of the styrene is inaccessible.⁷

Interestingly, these reactions of benzaldehyde appear to be both less stereoselective and less regioselective† than those of acetaldehyde. This situation contrasts with the singlet and triplet [2+2] photocycloadditions of diphenylvinylene carbonate to conjugated dienes, where the triplet state shows low stereoselectivity but high regioselectivity.⁸

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† Oxetans analogous to (13) and (16) form only 11% of the adducts from acetaldehyde and 2-methyl-1-phenylpropene.

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